

Table 3-7. Concentrations of radionuclides  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$ ,  $^{144}\text{Ce}$ ,  $^{137}\text{Cs}$ , and  $^{60}\text{Co}$  in new samples taken from cores collected during 1976-77 (from Humphrey, 1980; table 2)

[Analysis performed at the Radiological and Environmental Sciences Laboratory. Sample depth is in meters. Concentrations are in microcuries per gram times  $10^{-9}$  ( $10^{-9}$   $\mu\text{Ci/g}$ ) for  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ , and  $^{241}\text{Am}$  and in microcuries per gram times  $10^{-8}$  ( $10^{-8}$   $\mu\text{Ci/g}$ ) for  $^{90}\text{Sr}$ ,  $^{144}\text{Ce}$ ,  $^{137}\text{Cs}$ , and  $^{60}\text{Co}$ ]

Sample no.	Sample depth	$^{238}\text{Pu}$	$^{239,240}\text{Pu}$	$^{241}\text{Am}$	$^{90}\text{Sr}$	$^{144}\text{Ce}$	$^{137}\text{Cs}$	$^{60}\text{Co}$
76-1-1A	9.54	0.2±0.8	-0.043±0.45	-0.025±0.86	-1±4	-13±5	-2±2	0±2
76-1-2A	68.34	-0.023±1.2	-0.7±0.6	-0.34±1.2	-6±4	30±20	-2±5	-3±5
76-1-3A	69.01	-0.005±0.72	1.3±0.8	-0.3±1.3	-1±3	9±14	-3±4	-2±3
76-1-4A	69.43	0.6±0.7	0.031±0.53	0.38±1.1	4±4	-9±8	-4±4	-5±3
76-1-5A	69.59	-0.1±0.9	-0.4±0.5	0.37±1.0	7±4	14±9	1±2	0.9±2
76-2-1A	68.70	-0.009±0.63	0.6±0.8	-0.57±1.9	-3±3	-9±8	0±1.4	-3±3
76-2-2A	69.19	-0.8±0.7	0.2±0.6	0.074±0.94	1±3	-10±6	3±2	0.4±2
76-2-3A	71.14	-0.6±0.7	0.1±0.5	1.3±1.0	-5±3	10±10	-1±2	0.6±2
76-2-4A	71.69	0.3±0.5	-0.5±0.6	0.9±1.0	3±3	-9±8	-1±2	3±2
76-2-5A	72.97	-0.3±0.6	-0.5±0.5	-0.001±0.69	4±3	-2±7	-5±3	0±2
76-2-6A	73.97	2.0±1.0	0.5±0.6	-0.0±0.1	1±3	-20±7	-3±3	3±3
76-3-1A	30.27	-0.036±0.77	-0.04±0.02	0.55±1.0	2±4	-3±8	2±2	1±2
76-3-2A	31.85	-0.03±0.78	-0.7±0.6	0.6±0.9	1±3	13±13	7±4	-2±3
76-3-3A	32.40	0.1±0.4	0.1±0.4	0.2±0.7	4±4	-6±8	-1±1	0±2
76-3-4A	34.75	-0.6±0.5	0.2±0.1	0.1±1.0	5±3	-8±6	1±2	3±2
76-3-5A	35.36	-0.024±0.45	-0.7±0.5	-0.2±0.1	-1±3	-7±8	2±4	-1±2
76-3-6A	68.88	1.5±0.9	0.6±0.7	-1.4±0.9	-5±3	10±10	0±2	0±2
76-3-7A	70.81	-0.4±0.6	-0.4±0.5	10±10	2±3	-4±8	2±3	-4±3
76-3-8A	71.60	-0.45±0.45	-0.45±0.45	0.36±1.2	0±3	-2±8	0.5±2	1±1
76-3-9A	73.12	0.005±0.53	0.005±0.45	-0.3±0.6	-2±3	-1±6	-4±2	-5±2
76-4-1A	7.01	-0.4±0.5	-0.4±0.5	3.0±2.0	4±3	3±13	0.4±2	-2±2
76-4-2A	30.33	-0.6±0.9	0.003±0.33	0.4±1.0	-5±4	0.7±8	2±2	-2±2
76-4A-1A	69.49	0.1±1.0	0.007±0.52	0.033±0.93	5±3	-2±9	-5±4	-5±3
76-4A-2A	70.29	-0.9±0.6	-0.1±0.6	1.0±1.0	6±3	2±9	2±2	-8±4
76-4A-3A	71.14	0.2±0.7	0.2±0.5	0.018±0.94	2±3	-9±6	-2±2	0±2
76-4A-4A	72.05	1.1±0.7	-0.5±0.6	0.58±1.2	1±3	4±6	-1±2	0±2
76-4A-5A	73.03	0.2±0.8	-0.006±0.66	1.2±0.9	-3±3	7±14	1±3	-7±4
76-4A-6A	73.82	0.2±0.7	-0.029±0.45	0.4±0.8	4±3	-8±8	-2±4	-1±3
76-4A-7A	74.19	0.8±0.8	0.083±0.58	-0.1±0.7	-2±4	0±8	1±2	0±2

### 3-22 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-7. Concentrations of radionuclides  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$ ,  $^{144}\text{Ce}$ ,  $^{137}\text{Cs}$ , and  $^{60}\text{Co}$  in new samples taken from cores collected during 1976-77 (from Humphrey, 1980; table 2)—Continued

Sample no.	Sample depth	$^{238}\text{Pu}$	$^{239,240}\text{Pu}$	$^{241}\text{Am}$	$^{90}\text{Sr}$	$^{144}\text{Ce}$	$^{137}\text{Cs}$	$^{60}\text{Co}$
76-5-1A	30.60	-0.016±0.72	-0.02±0.02	1.0±1.0	4±3	-7±8	2±2	3±2
76-5-2A	30.97	0.065±0.9	0.4±1.0	0.47±1.0	1±4	-11±8	-4±3	-4±2
76-5-3A	32.49	-0.005±0.4	0.3±0.4	0.4±0.8	-2±4	-10±20	3±2	-1±2
76-5-4A	33.07	0.01±0.61	0.009±0.53	0.5±0.8	5±3	-13±6	-5±2	2±2
76-5-5A	34.99	0.2±0.7	-0.7±0.6	-0.88±1.2	7±4	14±13	4±2	-4±3
76-5-6A	68.64	0.027±0.45	-0.6±0.6	0.1±0.8	-6±4	25±13	-1±2	-2±2
76-5-7A	70.20	-0.4±0.5	-0.4±0.5	1.1±1.0	-1±4	-1±7	1±2	0.4±2
76-5-8A	71.41	0.3±0.6	0.2±0.6	1.4±1.0	2±3	-2±6	4±2	-1±2
76-5-9A	73.82	-0.7±0.6	-0.5±0.6	-0.8±0.8	5±3	-7±8	-2±2	4±2
76-6-1A	71.54	-0.3±0.9	0.2±0.5	-0.003±0.92	1±4	0±20	-1±3	-8±3
76-6-2A	72.02	0.2±0.5	-0.5±0.5	0.5±0.9	-3±4	6±12	2±2	-1±3

Table 3-8. Concentrations of radionuclides  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$ , and  $^{137}\text{Cs}$  in sediment samples collected in 1987 from wells D-02, D-06A, and TW-1 (from Laney and others, 1988; table 20)[Analysis by EG&G Idaho, Incorporated. Sample depth is in feet-inches. Concentrations are in microcuries per gram ( $\mu\text{Ci/g}$ ). Symbol: \* = sample result positive,  $>3\sigma$ ]

Sample	Sample depth interval	$^{238}\text{Pu}$		$^{239,240}\text{Pu}$		$^{241}\text{Am}$		$^{90}\text{Sr}$		$^{137}\text{Cs}$	
		Result	Exponent	Result	Exponent	Result	Exponent	Result	Exponent	Result	Exponent
Deep Hole D-02											
D-13	1-2 to 1-8	2.6±0.2	E-07*	1.13±0.05	E-06*	1.52±0.06	E-06*	1.9±0.3	E-07*	7.2±1.0	E-08*
D-17	9-2 to 9-8	6±9	E-10	0.6±1.1	E-09	0.3±1.2	E-09	-2±3	E-08	1±8	E-09
D-20	15-6 to 16-0	1.49±0.18	E-08*	2.55±0.09	E-07*	5.0±0.5	E-08*	1.3±0.3	E-07*	10±7	E-09
D-30	233-10 to 224-4	1.3±1.3	E-09	8±9	E-10	-0.1±1.0	E-09	-2±4	E-08	-2±8	E-09
D-31	224-4 to 226-4	2.6±1.1	E-09	7±8	E-10	0.0±1.2	E-09	2±3	E-08	4±7	E-09
D-34 (field split)	230-0 to 230-4	6.5±1.9	E-09*	0.8±1.0	E-09	0.3±1.3	E-09	4±3.0		-0±7	E-09
D-34 (lab split)	230-0 to 230-4	3.22±0.17	E-08*	5.8±0.2	E-08*						
D-34 (lab split 4,000-min. count)	230-0 to 230-4	1.5±0.4	E-09*	2±3	E-10						
D-34 (lab split 4,000-min. count)	230-0 to 230-4	3.3±0.6	E-09*	3±4	E-10						
D-34A (field split 4,000-min. count)	229-8 to 230-0	2.4±0.7	E-09*	3±6	E-10						
D-34A (lab split )	229-8 to 230-0	1.3±1.1	E-09	-3±7	E-10						
D-34A (lab split )	229-8 to 230-0	1.4±1.1	E-09	4±6	E-10						
D-35	232-3 to 232-7	1.6±1.7	E-09	1.1±1.0	E-09	-0.2±1.2	E-09	2±3	E-08	7±7	E-09
D-36	233-9 to 234-2	1.8±1.5	E-09	1.1±1.4	E-09	-0.3±1.2	E-09	2±4	E-08	0±6	E-09
D-37	234-9 to 235-2	1.4±1.1	E-09	1.0±0.9	E-09	0.2±1.4	E-09	-3±4	E-08	1.3±0.7	E-08

Table 3-8. Concentrations of radionuclides  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$ , and  $^{137}\text{Cs}$  in sediment samples collected in 1987 from wells D-02, D-06A, and TW-1 (from Laney and others, 1988; table 20)—Continued

Sample	Sample depth interval	<sup>238</sup> Pu			<sup>239,240</sup> Pu			<sup>241</sup> Am			<sup>90</sup> Sr			<sup>137</sup> Cs		
		Result	Exponent		Result	Exponent		Result	Exponent		Result	Exponent		Result	Exponent	
Deep Hole D-06A																
D-29	47-0 to 49-0	1.5±1.2	E-09		7±7	E-10		-2±9	E-10		4±3	E-08		5±2	E-08	
Deep Hole TW-1																
D-42 (field split)	101-0 to 101-2	1.7±0.2	E-08*		7.4±0.4	E-07*		4.4±0.2	E-07*		5±4	E-08				
D-42 (lab subsplit)	101-0 to 101-2	1.18±0.17	E-08*		6.1±0.3	E-07*		4.7±0.2	E-07*							
D-43A (field split)	101-2 to 101-7	4.6±1.4	E-09*		1.97±0.13	E-07*		1.03±0.08	E-07*		4±3	E-08				
D-43 (field subsplit)	101-2 to 101-7	6.3±1.7	E-09*		1.9±0.13	E-07*		1.06±0.09	E-07*							
D-43A (lab subsplit)	101-2 to 101-7	6.5±1.6	E-09*		2.00±0.13	E-07*		1.37±0.11	E-07*							
D-47	225-9 to 225-11	-4±6	E-10		8±7	E-10		2±9	E-10		6±3	E-08				
D-47 (lab subsplit)	225-9 to 225-11	7±7	E-10		2±6	E-10		0.5±1.0	E-09							
D-48	226-10 to 227-7	0.8±1.1	E-09		3±6	E-10		1.2±1.4	E-09		3±3	E-08		3±1.6	E-08	
D-48 (lab subsplit)	226-10 to 227-7	5±9	E-10		2±7	E-10		0.7±1.1	E-09							
D-48 (lab subsplit)	226-10 to 227-7	6±7	E-10		7±7	E-10		0.6±1.2	E-09							

Table 3-9. Comparison of results obtained by EG&G (table 3-8) with results obtained by the Radiological and Environmental Sciences Laboratory for radionuclides  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ , and  $^{241}\text{Am}$  in samples from well TW-1, B-C interbed (modified from Laney and others, 1988; table 21)

[Sample depths are in feet-inches. Concentrations are in microcuries per gram ( $\mu\text{Ci/g}$ ). Abbreviations: EGG = EG&G; RESL = Radiological and Environmental Sciences Laboratory; Symbol: \* = sample result statistically positive  $>3\sigma$ ; ND = presumably not detected]

Sample no.	Depth	EGG			RESL		
		$^{238}\text{Pu}$	$^{239,240}\text{Pu}$	$^{241}\text{Am}$	$^{238}\text{Pu}$	$^{239,240}\text{Pu}$	$^{241}\text{Am}$
D-43A	101-2	4.6 $\pm$ 1.4	E-09* 1.97 $\pm$ 0.13	E-07* 1.3 $\pm$ 0.08	E-08*† 10 $\pm$ 3	E-09* 1.78 $\pm$ 0.13	E-07* 8.47 $\pm$ 0.95
D-43A (lab subsplit)	101-2	6.3 $\pm$ 1.7	E-09* 1.90 $\pm$ 0.13	E-07* 1.06 $\pm$ 0.09	E-07* ND	1.68 $\pm$ 0.09	E-07* 9.08 $\pm$ 0.075
D-43A (lab subsplit)	101-2	6.5 $\pm$ 1.6	E-09* 2.00 $\pm$ 0.13	E-07* 1.37 $\pm$ 0.11	E-07* 3.9 $\pm$ 1.3	E-09 1.7 $\pm$ 0.09	E-07* 1.07 $\pm$ 0.09

† Value here does not match that given for D43A (field subsplit) in Laney and others, 1988, table 20 [1.03  $\pm$  0.08 E-07]

### 3-26 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-10. Summary of statistically significant ( $>3\sigma$ ) concentrations for waste radionuclides in samples from selected depth intervals and wells

- A: Interval 1, 10 to 75 ft (3 to 23 m) below land surface.
- B: Interval 2, 82 to 142 ft (25 to 43 m) below land surface.
- C: Interval 3, 217 to 265 ft (66 to 81 m) below land surface.
- D. Background sites

#### Summary of statistically positive results

Table 3-10A, B, C, and D is a modification of a summary table by Dames and Moore (1992, table 5-5, -6, -7, and -8, hereafter called D/M SUM) which presents data for statistically positive results determined by using the 3s criteria. The 1992 report was revised in 1994 (Dames and Moore, 1994); however only appendix A of the 1994 report (APX-94) was available for the preparation of this report. The picocurie units in appendix A of the 1992 report (APX-92) were changed to nanocurie units to correct a major (3 orders of magnitude) conversion error. Other than the change in units, the statistically positive results in APX-94 are the same (with two exceptions) as in APX-92, which was used to prepare the D/M SUM. Data presented in this table (table 3-10) reflect the corrections made in APX-94. In addition to the conversion error, other discrepancies were found among the data from the D/M SUM, APX-92 and APX-94 (D/M APX), and tables in several reports in which results for the selected samples were first presented (tables 3-1 to 3-9 of this report). Samples for which there are discrepancies are listed in boldface type, and results from each of the three data sources (D/M SUM, D/M APX, and the original tables) are listed. The type of discrepancy is documented in the "Discrepancy" column (see below for explanation of discrepancies). Where there are differences among the tables, the original reports are assumed to be correct.

Statistically positive results listed in the D/M APX from above 10 feet (3 meters) and below 500 feet (152 meters) below land surface are not in the D/M SUM and are not included in table 3-10. Some information that is not in the D/M SUM was added to table 3-10 (year, depth interval, analytical laboratory, and replication). Data from D/M SUM were reordered so that samples are listed by year in table 3-10. Samples that have statistically positive results are grouped by well and also by depth interval. Dashed lines (---) indicate that data for the well interval are not presented in table 3-10. Where the depth listed in the D/M SUM is different from that listed in the original report, the depth from the original report is listed in parentheses. Statistically positive results for replicate samples are listed consecutively and indicated by a letter (A, B, etc.) in the Replicates column. Statistically negative results for replicate samples are indicated by a number in the Replicates representing the number of negative analyses. Below this number, the statistically negative values are listed. "No" in the Replicates column indicates that no replicates were analyzed. In some cases, the replicates were analyzed in a different laboratory. The analyzing laboratories are abbreviated in the Lab column as follows: RESL, Radiological and Environmental Sciences Laboratory (formerly Idaho National Engineering Laboratory Health Service Laboratory); ACC, Allied Chemical Corporation; and EGG, EG&G.

#### Types of errors found:

- 0 Data verified against data in appendix A and the original report, except for probable rounding errors.
- 1 Data on Dames and Moore summary table does not agree with appendix A: uncertainty incorrect.
- 2 Data on Dames and Moore summary table does not agree with appendix A: exponent(s) incorrect; 2a both the value and uncertainty incorrect; 2b either value or uncertainty incorrect.
- 3 Error corrected in Dames and Moore, rev. 3 appendix A.
- 4 Dames and Moore summary table does not agree with appendix A: well listed incorrectly.
- 5 Statistically positive value not listed in Dames and Moore summary table.
- 6 Data listed in appendix A does not agree with data in original report.
- 7 The original report (Laney and others, 1988) states that EGG values from Table 20 have been used to prepare Table 21, however Am-241 value (nCi/g)  $1.3 \pm 0.08 \text{ E-5}$  in Table 21 does not agree with  $1.03 \pm 0.08 \text{ E-4}$  in Table 20. The former value appears in App. A (1992) and has been changed to the latter value in App A, Rev. 3. Pu-238 value is (nCi/g)  $1.18 \pm 0.17 \text{ E-5}$  in Table 20 and  $1.18 \pm 0.17 \text{ E-4}$  in Table 21.
- 8 Not statistically positive
- \* Verification not possible because 1979 original report is unavailable.

Table 3-10A. Interval 1 (10 to 75 feet (3 to 23 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-5), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision) and data from the original reports, tables 3-1 through 3-9 (this report)

[Concentrations are in nanocuries per gram (nCi/g). Abbreviations: D/M SUM = Dames and Moore (1992, table 5-5); D/M APX = Dames and Moore (1992 and 1994 revision) Appendix A; ORIGINAL = Data from original reports, tables 3-1 through 3-9 (this report)]

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1972	USGS 93	13.83-14.00	<sup>90</sup> Sr	D/M SUM	4.00E-04	9.00E-05	RESL	NO	0
1972	USGS 93	13.83-14.00	<sup>241</sup> Am	D/M SUM	1.20E-05	3.00E-06	RESL	NO	1, 8
				D/M APX	1.20E-05	3.00E-06			
				ORIGINAL	1.20E-05	4.50E-06			
1987	D-O2	15.50-16.00	<sup>241</sup> Am	D/M SUM	5.00E-05	5.00E-06	EGG	NO	0
1987	D-O2	15.50-16.00	<sup>238</sup> Pu	D/M SUM	1.49E-04	1.80E-05	EGG	NO	2a
				D/M APX	1.49E-05	1.80E-06			
				ORIGINAL	1.49E-05	1.80E-06			
1987	D-O2	15.50-16.00	<sup>239,240</sup> Pu	D/M SUM	2.55E-04	9.00E-06	EGG	NO	0
1987	D-O2	15.50-16.00	<sup>90</sup> Sr	D/M SUM	1.30E-04	2.00E-05	EGG	NO	1
				D/M APX	1.30E-04	3.00E-05			
				ORIGINAL	1.30E-04	3.00E-05			

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)

[Concentrations are in nanocuries per gram (nCi/g)]

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1971	USGS 88	111.00-112.5	<sup>239,240</sup> Pu	D/M SUM	1.00E-05	0.00E+00	RESL	NO	8
				D/M APX	1.00E-05	---			
				ORIGINAL	---	---			
1972	USGS 93	98.00-101.00	<sup>60</sup> Co	D/M SUM	6.20E-05	1.20E-05	RESL	NO	0
1972	USGS 93	98.00-101.00	<sup>239,240</sup> Pu	D/M SUM	1.10E-04	7.00E-06	RESL	NO	0
1972	USGS 93	98.00-101.00	<sup>238</sup> Pu	D/M SUM	---	---			5
				D/M APX	7.60E-06	1.50E-06			
				ORIGINAL	8.00E-06	1.50E-06			
1972	USGS 93	98.00-101.00	<sup>137</sup> Cs	D/M SUM	1.00E-04	2.00E-05	RESL	NO	0
1972	USGS 93	101.00-103.00	<sup>241</sup> Am	D/M SUM	6.30E-05	1.00E-05	RESL	A	0
1972	USGS 93	101.00-103.00	<sup>241</sup> Am	D/M SUM	1.50E-04	2.00E-05	RESL	B	0
1972	USGS 93	101.00-103.00	<sup>239,240</sup> Pu	D/M SUM	5.40E-04	1.20E-05	RESL	A	0
1972	USGS 93	101.00-103.00	<sup>239,240</sup> Pu	D/M SUM	2.30E-04	1.10E-05	RESL	B	0
1972	USGS 93	101.00-103.00	<sup>238</sup> Pu	D/M SUM	---	---	RESL	A	5
				D/M APX	1.40E-05	3.00E-06			
				ORIGINAL	1.40E-05	3.00E-06			



Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)---Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1972	USGS 93	101.00-103.00	$^{238}\text{Pu}$	D/M SUM	---	---	RESL	B	5
				D/M APX	8.60E-06	3.00E-06			
				ORIGINAL	9.00E-06	3.00E-06			
1972	USGS 93	101.00-103.00	$^{90}\text{Sr}$	D/M SUM	6.90E-04	1.10E-04	RESL	NO	0
1972	USGS 93	103.00-105.00	$^{90}\text{Sr}$	D/M SUM	4.00E-04	1.10E-04	RESL	NO	0
1972	USGS 93	103.00-105.00	$^{241}\text{Am}$	D/M SUM	4.50E-05	4.00E-06	RESL	NO	1
				D/M APX	4.50E-05	6.00E-06			
				ORIGINAL	4.50E-05	6.00E-06			
1972	USGS 93	103.00-105.00	$^{239,240}\text{Pu}$	D/M SUM	8.10E-05	1.10E-06	RESL	NO	2b
				D/M APX	8.10E-05	1.10E-05			
				ORIGINAL	8.10E-05	1.10E-05			
1972	USGS 92	88.5-90	$^{90}\text{Sr}$	D/M SUM	3.00E-04	9.00E-05	RESL	NO	0
1972	USGS 94	95.92-102	$^{90}\text{Sr}$	D/M SUM	1.50E-04	5.00E-05	RESL	NO	0
1972	USGS 96	100.50-101	$^{239,240}\text{Pu}$	D/M SUM	4.50E-05	2.00E-07	RESL	NO	2b
				D/M APX	4.50E-05	2.00E-06			
				ORIGINAL	4.50E-05	2.00E-06			

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1972	USGS 96	100.50-101	<sup>238</sup> Pu	D/M SUM	---	---	RESL	NO	5
				D/M APX	5.90E-06	1.50E-06			
				ORIGINAL	6.00E-06	1.50E-06			
	USGS 96	110.00-112.92	<sup>241</sup> Am	D/M SUM	---	---	RESL	A	5, 6
				D/M APX	2.30E-05	2.00E-05			
				ORIGINAL	2.30E-04	2.00E-05			
1972	USGS 96	110.00-112.92 (110.00-110.50)	<sup>241</sup> Am	D/M SUM	3.00E-05	6.00E-06	RESL	B	0
1972	USGS 96	122.75-124.75	<sup>137</sup> Cs	D/M SUM	---	---	RESL	NO	5
				D/M APX	5.50E-04	4.00E-05			
				ORIGINAL	5.50E-04	4.00E-05			
1972	USGS 95	112.00-113.33	<sup>137</sup> Cs	D/M SUM	2.20E-04	1.00E-05	RESL	NO	0
1976	76-4A	97.8	<sup>241</sup> Am	D/M SUM	6.40E-06	1.70E-06	RESL	2 (0.0±1.0E-6) (0.0±1.0E-6)	0
1976	76-3	97.50-97.80	<sup>241</sup> Am	D/M SUM	8.40E-06	1.40E-06	ACC	1 (-1.0±1.0E-6)	0

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1976	76-3	97.50-97.80	$^{239,240}\text{Pu}$	D/M SUM	---	---	RESL	1	5
				D/M APX	1.68E-05	5.00E-06		(0.0±1.0E-6)	
				ORIGINAL	1.68E-05	5.00E-06			
1978	78-5	101.71	$^{238}\text{Pu}$	D/M SUM	---	---	RESL	1	5
		(31.00 m)		D/M APX	3.10E-06	1.00E-06		(1.7±0.8E-6)	
				ORIGINAL	3.10E-06	1.00E-06			
1979	79-2	99.11-99.90	$^{241}\text{Am}$	D/M SUM	2.20E-05	2.00E-06	*	A	*
1979	79-2	99.11-99.90	$^{241}\text{Am}$	D/M SUM	3.10E-05	3.00E-06	*	B	*
1979	79-2	99.11-99.90	$^{239,240}\text{Pu}$	D/M SUM	---	---	*	A	5, *
				D/M APX	6.10E-05	4.00E-06			
				ORIGINAL	*	*			
1979	79-2	99.11-99.90	$^{239,240}\text{Pu}$	D/M SUM	---	---	*	B	5, *
				D/M APX	5.60E-05	4.00E-06			
				ORIGINAL	*	*			
1979	79-2	99.90-101.71	$^{241}\text{Am}$	D/M SUM	1.30E-05	3.00E-06	*	A	*
1979	79-2	99.90-101.71	$^{241}\text{Am}$	D/M SUM	1.80E-05	2.00E-06	*	B	*
1979	79-2	99.90-101.71	$^{239,240}\text{Pu}$	D/M SUM	---	---	*	A	5, *
				D/M APX	3.40E-05	3.00E-06			
				ORIGINAL	*	*			

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1979	79-2	99.90-101.71	$^{239,240}\text{Pu}$	D/M SUM	---	---	*	B	5, *
				D/M APX	3.70E-05	3.00E-06			
				ORIGINAL	*	*			
1979	79-2	101.71-102.99	$^{239,240}\text{Pu}$	D/M SUM	---	---	*	A	5, *
				D/M APX	3.80E-05	3.00E-06			
				ORIGINAL	*	*			
1979	79-2	101.71-102.99	$^{239,240}\text{Pu}$	D/M SUM	---	---	*	B	5, *
				D/M APX	3.60E-05	3.00E-06			
				ORIGINAL					
1979	79-2	101.71-102.99	$^{241}\text{Am}$	D/M SUM	2.40E-05	3.00E-06	*	A	*
1979	79-2	101.71-102.99	$^{241}\text{Am}$	D/M SUM	2.00E-05	3.00E-06	*	B	*
1979	79-2	101.71-102.99	$^{60}\text{Co}$	D/M SUM	5.20E-05	1.70E-05	*	3	*
								(2±2E-5)	
								(-1±2E-5)	
								(-1±2E-5)	
1979	79-3	100.69-106.2	$^{60}\text{Co}$	D/M SUM	2.50E-04	2.00E-05	*	A	*
1979	79-3	100.69-106.2	$^{60}\text{Co}$	D/M SUM	2.80E-04	2.00E-05	*	B	*

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1987	TW-1	101.00-101.17	$^{239,240}\text{Pu}$	D/M SUM	---	---	EGG	A	5
				D/M APX	7.40E-04	4.00E-05			
				ORIGINAL	7.40E-04	4.00E-05			
1987	TW-1	101.00-101.17	$^{239,240}\text{Pu}$	D/M SUM	---	---	EGG	B	5
				D/M APX	6.10E-04	3.00E-05			
				ORIGINAL	6.10E-04	3.00E-05			
1987	TW-1	101.00-101.17	$^{241}\text{Am}$	D/M SUM	4.70E-04	2.00E-05	EGG	A	0
1987	TW-1	101.00-101.17	$^{241}\text{Am}$	D/M SUM	4.40E-04	2.00E-05	EGG	B	0
1987	TW-1	101.00-101.17	$^{238}\text{Pu}$	D/M SUM	---	---	EGG	A	5
		(101)		D/M APX	1.70E-05	2.00E-06			
				ORIGINAL	1.70E-05	2.00E-06			
1987	TW-1	101.00-101.17	$^{238}\text{Pu}$	D/M SUM	---	---	EGG	B	5, 7
		(101)		D/M APX	1.18E-05	1.70E-06			
				ORIGINAL	1.18E-05	1.70E-06			
1987	TW-1	101.17	$^{238}\text{Pu}$	D/M SUM	---	---	EGG	A	5
				D/M APX	4.60E-06	1.40E-06			
				ORIGINAL	4.60E-06	1.40E-06			

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1987	TW-1	101.17	$^{238}\text{Pu}$	D/M SUM	---	---	RESL	B	5
				D/M APX	1.00E-05	3.00E-06			
				ORIGINAL	1.00E-05	3.00E-06			
1987	TW-1	101.17	$^{238}\text{Pu}$	D/M SUM	---	---	EGG	C	5
				D/M APX	6.30E-06	1.70E-06			
				ORIGINAL	6.30E-06	1.70E-06			
1987	TW-1	101.17 (101.17-101.58)	$^{239,240}\text{Pu}$	D/M SUM	---	---	EGG	A	5
				D/M APX	1.97E-04	1.30E-05			
				ORIGINAL	1.97E-04	1.30E-05			
1987	TW-1	101.17 (101.17-101.58)	$^{239,240}\text{Pu}$	D/M SUM	---	---	RESL	B	5
				D/M APX	1.78E-04	1.30E-05			
				ORIGINAL	1.78E-04	1.30E-05			
1987	TW-1	101.17 (101.17-101.58)	$^{239,240}\text{Pu}$	D/M SUM	---	---	EGG	C	5, 3
				D/M APX	1.97E-04	1.30E-05			
				ORIGINAL	1.90E-04	1.30E-05			
1987	TW-1	101.17 (101.17-101.58)	$^{239,240}\text{Pu}$	D/M SUM	---	---	RESL	D	5
				D/M APX	1.68E-04	9.00E-06			
				ORIGINAL	1.68E-04	9.00E-06			

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1987	TW-1	101.17	$^{239,240}\text{Pu}$	D/M SUM	---	---	EGG	E	5
		(101.17-101.58)		D/M APX	2.00E-04	1.30E-05			
				ORIGINAL	2.00E-04	1.30E-05			
1987	TW-1	101.17	$^{239,240}\text{Pu}$	D/M SUM	---	---	RESL	F	5
		(101.17-101.58)		D/M APX	1.70E-04	9.00E-06			
				ORIGINAL	1.70E-04	9.00E-06			
1987	TW-1	101.17	$^{241}\text{Am}$	D/M SUM	1.37E-04	1.10E-05	EGG	A	0
1987	TW-1	101.17	$^{241}\text{Am}$	D/M SUM	1.00E-04	9.00E-06	RESL	B	0
1987	TW-1	101.17	$^{241}\text{Am}$	D/M SUM	1.30E-05	8.00E-06	EGG	C	1, 7
				D/M APX	1.30E-05	8.00E-07			
				ORIGINAL	1.30E-05	8.00E-07			
				ORIGINAL	1.03E-04	8.00E-06	EGG	C	5, 7
1987	TW-1	101.17	$^{241}\text{Am}$	D/M SUM	8.47E-05	9.50E-06	RESL	D	0
1987	TW-1	101.17	$^{241}\text{Am}$	D/M SUM	1.06E-04	9.00E-06	EGG	E	0
1987	TW-1	101.17	$^{241}\text{Am}$	D/M SUM	9.08E-04	7.00E-06	RESL	F	0

Table 3-10C. Interval 3 (217 to 285 feet (66 to 81 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-7), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)

[Concentrations are in nanocuries per gram (nCi/g)]

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1972	USGS 95	226.75-229.25	<sup>60</sup> Co	D/M SUM	2.40E-04	3.00E-05	RESL	NO	0
1972	USGS 95	226.75-229.25	<sup>137</sup> Cs	D/M SUM	2.30E-04	3.00E-05	RESL	NO	0
1972	USGS 94	262.25-264.58	<sup>60</sup> Co	D/M SUM	2.50E-04	3.00E-05	RESL	NO	0
1972	USGS 94	262.25-264.58	<sup>137</sup> Cs	D/M SUM	1.80E-04	3.00E-05	RESL	NO	0
1972	USGS 92	223.00-225.50	<sup>60</sup> Co	D/M SUM	2.30E-04	2.00E-05	RESL	NO	0
1972	USGS 92	223.00-225.50	<sup>137</sup> Cs	D/M SUM	1.30E-04	3.00E-05	RESL	NO	6
				D/M APX	1.30E-04	3.00E-06			
				ORIGINAL	1.30E-04	3.00E-05			
1972	USGS 92	223.00-225.50	<sup>90</sup> Sr	D/M SUM	3.00E-03	9.00E-04	RESL	NO	2a
				D/M APX	3.00E-04	9.00E-05			
				ORIGINAL	3.00E-04	9.00E-05			
1972	USGS 91	233.75-236.25	<sup>90</sup> Sr	D/M SUM	1.20E-04	1.00E-04	RESL	NO	2b
				D/M APX	1.20E-03	1.00E-04			
				ORIGINAL	1.20E-03	1.00E-04			



Table 3-10C. Interval 3 (217 to 265 feet (66 to 81 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-7), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1972	USGS 91	236.50-237.00	$^{239,240}\text{Pu}$	D/M SUM	1.40E-04	7.00E-05	RESL	NO	2b
				D/M APX	1.40E-04	7.00E-06			
				ORIGINAL	1.40E-04	7.00E-06			
1976	76-4A	226	$^{241}\text{Am}$	D/M SUM	2.30E-05	3.00E-06	RESL	2	0
								( $2.3 \pm 1.5\text{E-}6$ ) ( $-1.0 \pm 1.0\text{E-}6$ )	
1976	76-4	221	$^{90}\text{Sr}$	D/M SUM	4.90E-04	6.00E-05	RESL	A	4
				D/M APX	4.90E-04	6.00E-05			
				ORIGINAL	4.90E-04	6.00E-05			
1976	76-1	221.2	$^{90}\text{Sr}$	D/M SUM	4.20E-04	5.00E-05	RESL	B	0
1978	78-2	235.7 (71.84m)	$^{241}\text{Am}$	D/M SUM	3.30E-05	3.00E-06	RESL	1	0
								( $-0.31 \pm 1.3\text{E-}6$ )	
1978	78-3	226.9 (69.16m)	$^{137}\text{Cs}$	D/M SUM	7.00E-04	2.00E-05	RESL	1	2b
				D/M APX	7.00E-05	2.00E-05			
				ORIGINAL	7.00E-05	2.00E-05		( $0 \pm 3\text{E-}5$ )	
1978	78-6	242.39 (73.88m)	$^{90}\text{Sr}$	D/M SUM	1.20E-04	4.00E-05	RESL	1	4
				D/M APX	1.20E-04	4.00E-05			( $2 \pm 4\text{E-}5$ )
				ORIGINAL	1.20E-04	4.00E-05			

Table 3-10C. Interval 3 (217 to 265 feet (66 to 81 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-7), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

Year	Well	Depth (feet)	Radionuclide	Source	Concentration	Uncertainty	Anal. lab	Replicates	Error
1978	78-5	240.29 (73.24m)	<sup>239,240</sup> Pu	D/M SUM	1.30E-05	2.00E-06	RESL	1	0
1978	78-5	240.29 (73.24m)	<sup>238</sup> Pu	D/M SUM	3.00E-06	1.00E-07	RESL	1	2b
				D/M APX	3.00E-06	1.00E-06		(-0.9±0.7E-6)	
				ORIGINAL	3.00E-06	1.00E-06			
1987	D-O2	229.67-230.00	<sup>238</sup> Pu	D/M SUM	2.40E-06	7.00E-07	EGG	2	0
								(1.3±1.1E-6) (1.4±1.1E-6)	
1987	D-O2	230.00-230.33	<sup>238</sup> Pu	D/M SUM	1.50E-06	4.00E-07	EGG	A	0
1987	D-O2	230.00-230.33	<sup>238</sup> Pu	D/M SUM	6.50E-06	1.90E-07	EGG	B	2b
				D/M APX	6.50E-06	1.90E-06			
				ORIGINAL	6.50E-06	1.90E-06			
1987	D-O2	230.00-230.33	<sup>238</sup> Pu	D/M SUM	3.22E-05	1.70E-06	EGG	C	0
1987	D-O2	230.00-230.33	<sup>238</sup> Pu	D/M SUM	3.30E-06	6.00E-08	EGG	D	2b
				D/M APX	3.30E-06	6.00E-07			
				ORIGINAL	3.30E-06	6.00E-07			
1987	D-O2	230.00-230.33	<sup>239,240</sup> Pu	D/M SUM	5.80E-05	2.00E-06	EGG	3	0
								(0.8±1E-6) (2±3E-7) (3±4E-7)	

[Concentrations are in nanocuries per gram (nCi/g)]

[illegible]

### 3-40 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-11. Comparison of actinide data ( $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ , and  $^{241}\text{Am}$  from tables 3-1 through 3-9 of this report) for the B-C and C-D interbeds (modified from format of Navratil, 1996, table 4)

Description of Data	B-C interbed		C-D interbed	
	This study	Navratil 1996	This study	Navratil 1996
Number of wells showing statistically significant actinide ( $^{241}\text{Am}$ , $^{239,240}\text{Pu}$ and/or $^{238}\text{Pu}$ ) detection at 99-percent confidence level:	7 <sup>a</sup>	8 <sup>aa</sup>	5 <sup>b</sup>	9 <sup>bb</sup>
Number of wells showing statistically significant actinide ( $^{239,240}\text{Pu}$ and/or $^{238}\text{Pu}$ ) detection at 99-percent confidence level:	6 <sup>c</sup>	7 <sup>cc</sup>	3 <sup>d</sup>	6 <sup>dd</sup>
Number of post-1972 wells showing statistically significant actinide ( $^{241}\text{Am}$ , $^{239,240}\text{Pu}$ and/or $^{238}\text{Pu}$ ) detection at 99-percent confidence level:	5 <sup>e</sup>	6 <sup>ee</sup>	4 <sup>f</sup>	5 <sup>ff</sup>
Number of post-1972 wells showing statistically significant actinide ( $^{239,240}\text{Pu}$ and/or $^{238}\text{Pu}$ ) detection at 99-percent confidence level:	4 <sup>g</sup>	5 <sup>gg</sup>	2 <sup>h</sup>	2 <sup>hh</sup>
<b>This report</b>				
<sup>a</sup> 1972: wells USGS 93 and USGS 96	<sup>g</sup> 1976: well 76-3		<sup>dd</sup> 1971: wells USGS 87 and USGS 88	
1976: wells 76-4A and 76-3	1978: well 78-5		1972: wells USGS 91 and USGS 96	
1978: well 78-5	1979: well 79-2		1978: well 78-5	
1979: well 79-2	1987: well TW-1		1987: well D-O2	
1987: well TW-1	<sup>h</sup> 1978: well 78-5		<sup>ee</sup> 1976: wells 76-4A, and 76-3	
<sup>b</sup> 1972: well USGS 91	1987: well D-O2		1978: well 78-5	
1976: well 76-4A	<b>Navratil, 1996</b>		1979: well 79-2	
1978: wells 78-2 and 78-5	<sup>aa</sup> 1972: wells USGS 93 and USGS 96		1987: well TW-1	
1987: well D-O2	1976: wells 76-4A and 76-3		1988: well 88-01D	
<sup>c</sup> 1972: wells USGS 93 and USGS 96	1978: well 78-5		<sup>ff</sup> 1976: well 76-4A	
1976: well 76-3	1979: well 79-2		1978: wells 78-2 and 78-5	
1978: well 78-5	1987: well TW-1		1987: well D-O2	
1979: well 79-2	1988: well 88-01D		1989: well 89-01	
1987: well TW-1	<sup>bb</sup> 1971: wells USGS 87 and USGS 88		<sup>gg</sup> 1976: well 76-3	
<sup>d</sup> 1972: well USGS 91	1972: wells USGS 91 and USGS 96		1978: well 78-5	
1978: well 78-5	1976: well 76-4A		1979: well 79-2	
1987: well D-O2	1978: wells 78-2 and 78-5		1987: well TW-1	
<sup>e</sup> 1976: wells 76-4A and 76-3,	1987: well D-O2		1988: well 88-01D	
1978: well 78-5	1989: well 89-01		<sup>hh</sup> 1978: well 78-5	
1979: well 79-2	<sup>cc</sup> 1972: wells USGS 93 and USGS 96		1987: well D-O2	
1987: well TW-1	1976: well 76-3			
<sup>f</sup> 1976: well 76-4A	1978: well 78-5			
1978: wells 78-2 and 78-5	1979: well 79-2			
1987: well D-O2	1987: well TW-1			
	1988: well 88-01D			

Table 3-12. Actinide detections ( $^{241}\text{Am}$ ,  $^{238}\text{Pu}$ , and  $^{239,240}\text{Pu}$ ) reported in tables 3-1 through 3-9 of this report from the B-C interbed (modified from format of Navratil, 1996, table 2)

[Concentrations are in nanocuries per gram (nCi/g). Values shown are from original tables. Symbols: \* = one result at the 99-percent confidence level and one non-detect duplicate; \*\* = one result at the 99-percent confidence level; \*\*\* = multiple results at the 99-percent confidence level]

Well	$^{241}\text{Am}$		$^{238}\text{Pu}$		$^{239,240}\text{Pu}$	
	Results	Concentration (with exponent)	Results	Concentration (with exponent)	Results	Concentration (with exponent)
USGS 93 (1972)	***	6.3±1.0 E-5	***	8±1.5 E-6	***	1.1±0.07 E-4
		1.5±0.2 E-4		1.4±0.3 E-5		8.1±1.1 E-5
		4.5±0.6 E-5		9±3 E-6		5.4±0.12 E-4
						2.3±0.11 E-4
USGS 96 (1972)	*	3±0.6 E-5	**	6±1.5 E-6	**	4.5±0.2 E-5
76-3 (1976)	*	8.4±1.4 E-6			*	1.68±0.5 E-5
76-4A (1976)	*	6.4±1.7 E-6				
78-5 (1978)			*	3.1±1 E-6		
79-2 (1979)	***	2.2±0.2 E-5			***	6.1±0.4 E-5
		3.1±0.3 E-5				5.6±0.4 E-5
		1.3±0.3 E-5				3.4±0.3 E-5
		1.8±0.2 E-5				3.7±0.3 E-5
		2.4±0.3 E-5				3.8±0.3 E-5
		2±0.3 E-5				3.6±0.3 E-5
TW-1	***	4.7±0.2 E-4	***	1.7±0.2 E-5	***	7.4±0.4 E-4
		4.4±0.2 E-4		1.18±0.17 E-5		6.1±0.3 E-4
		1.37±0.11 E-4		4.6±1.4 E-6		1.97±0.13 E-4
		1.07±0.09 E-4		10±3 E-6		1.78±0.13 E-4
		1.3±0.08 E-5		6.3±1.7 E-6		1.9±0.13 E-4
		8.47±0.95 E-5		6.5±1.6 E-6		1.68±0.09 E-4
		1.06±0.09 E-4		3.9±1.3 E-6		2±0.13 E-4
		9.08±0.08 E-4				1.7±0.09 E-4
		1.03±0.08 E-4				

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Table 3-13. Actinide detections ( $^{241}\text{Am}$ ,  $^{238}\text{Pu}$ , and  $^{239,240}\text{Pu}$ ) reported in tables 3-1 through 3-9 of this report from the C-D interbed(modified from format of Navratil,1996, table 3)

[Values shown are from the original reports. Concentrations are shown in nanocuries per gram (nCi/g). Symbols: \* = one result at the 99-percent confidence level and one non-detect duplicate; \*\* = one result at the 99-percent confidence level; and \*\*\* = multiple results at the 99-percent confidence level]

Well	$^{241}\text{Am}$		$^{238}\text{Pu}$		$^{239,240}\text{Pu}$	
	Results	Concentration (with exponent)	Results	Concentration (with exponent)	Results	Concentration (with exponent)
USGS 91 (1972)					**	$1.4 \pm 0.07 \text{ E-4}$
76-4A (1976)	*	$2.3 \pm 0.3 \text{ E-5}$				
78-2 (1978)	*	$3.3 \pm 0.3 \text{ E-5}$				
78-5 (1978)			*	$3 \pm 1 \text{ E-6}$	*	$1.3 \pm 0.2 \text{ E-5}$
D-O2 (1987)			***	$2.4 \pm 0.7 \text{ E-6}$	*	$5.8 \pm 0.2 \text{ E-5}$
				$1.5 \pm 0.4 \text{ E-6}$		
				$6.5 \pm 1.9 \text{ E-6}$		
				$3.22 \pm 0.17 \text{ E-5}$		
				$3.3 \pm 0.6 \text{ E-6}$		

## 4.0 Task 2: Actinide transport processes

### 4.1 Introduction

The purpose of this chapter is to propose explanations for the reported detections of actinides in the subsurface at the Subsurface Disposal Area (SDA). The contractor provided selected historically reported detections of actinides in the subsurface at the SDA which are summarized in chapter 3. In that discussion, it was noted that the question of whether the reported detections were the result of cross contamination related to borehole drilling or the result of migration in ground-water flow was unresolvable. The possibility of cross contamination will not be discussed further in this chapter. Flow in the fractured rocks and sedimentary interbeds below the SDA was discussed in chapter 2. Chapter 2 notes that there are several kinds of preferential flow at the SDA: (1) macropore flow, (2) funneled flow, and (3) unstable flow. These different kinds of preferential flow could enhance migration of water and dissolved solutes. Transport of actinides in all cases is affected to some degree by the reactions between the actinides and solid surfaces and colloids. This chapter considers explanations of reported detections that involve reactive transport of actinides with the movement of water as the result of infiltration and recharge and includes geochemical effects such as adsorption, colloidal transport, and nonequilibrium effects.

### 4.2 Summary of geochemical characteristics at the Subsurface Disposal Area

The geochemical and lithological settings at the SDA are discussed in chapter 2. Geochemical characteristics at the site can have a large effect on some or all of the actinides considered. Specifically, water from perched zones below the SDA and from the Snake River Plain (SRP) aquifer have the following characteristics that can significantly affect actinide transport: (1) a pH that ranges from 7.8 to 8.4, (2) dissolved oxygen concentrations that are nearly saturated to slightly supersaturated with respect to air, (3) saturation indices that indicate the water is typically nearly saturated with respect to calcite, and (4) dissolved organic carbon (DOC) concentrations that are generally smaller than 1 mg/L (Knobel and others 1992a) or about 1 mg/L (Busenberg, USGS written commun., 1999). Generally, larger DOC concentrations are in water from wells that are contaminated by drilling-fluid surfactants or show evidence of other anthropogenic organic contamination (Busenberg, verbal commun.,

1999). In a previous study (Leenheer and Bagby, 1982) significantly larger DOC concentrations were measured in INEEL ground waters; concentrations ranged from 1.6 to 18 mg/L.

Investigations of cores collected at the site indicate that (1) calcite commonly occurs both in fractures and in the sedimentary interbeds, (2) iron oxyhydroxides, which can adsorb actinides strongly in certain conditions, are commonly observed on fracture surfaces and in the interbed sediments, and (3) clay minerals, most commonly identified as illite, account for an average of 20 percent of the interbed sediments analyzed (Bartholomay, 1990c). Both smectite and mixed-layer smectite clays were also observed in some interbed samples. These characteristics define an environment that controls the geochemical processes that affect actinide mobility. For example, the presence of oxygen and carbon impact the oxidation/reduction characteristics of the system. The oxidation/reduction conditions control the redox state of most actinides which affects the affinity of the chemical species for the aqueous or solid phase. The mineralogy, size, consolidation, and fracture pattern of the solid-phase matrix and the chemical composition of the aqueous solution will impact the rate and amount of sorption and subsequent solute transport. Section 4.3.1 discusses the speciation characteristics of Am, U, Np, and Pu and the effect on mobility of each in SDA ground water. First, however, the potential effects of speciation on transport are discussed by considering a simplified example (section 4.3). Section 4.4 discusses the effects of chemically mediated and transport controlled kinetics on sorption and desorption reactions, and section 4.5 discusses colloid facilitated transport of actinides.

### 4.3 Potential effects of speciation on actinide transport

A simple approach for describing adsorption of an actinide to subsurface solids is to use a distribution coefficient, or  $K_d$  value.  $K_d$  is the ratio of the concentration of adsorbed solute to the concentration of dissolved solute:

$$K_d = \frac{C_s}{C_{Aq}} \quad (4.1)$$

where:

$K_d$  = distribution coefficient, in volume per mass;  
 $C_s$  = mass of solute adsorbed per mass of adsorbent; and  
 $C_{Aq}$  = mass of solute dissolved per volume of water.

The commonly used retardation factor ( $R_F$ ) is defined by the equation

#### 4-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

$$R_F = 1 + \frac{P_b}{\theta} K_d \quad (4.2)$$

where:

$P_b$  = bulk density of the porous medium, in mass per volume;

$\theta$  = water filled porosity, in volume water per volume pore space; and

$R_F$  = ratio of the velocity of a linearly sorbing chemical to the velocity of a conservatively transported solute.

The term  $\frac{P_b}{\theta}$  can be thought of as a conversion factor necessary so that the concentrations of the sorbed solute are expressed in the same units as those for concentration of the dissolved solute. In other words, the concentrations of sorbed solutes are expressed as mass sorbed per volume (or mass) of water. It is convenient to define a new distribution coefficient as:

$$K_r = \frac{C_s (\text{mol sorbed/L (or Kg) water})}{C_{Aq} (\text{mol dissolved/L (or Kg) water})} \quad (4.3)$$

where:

$K_r$  = distribution coefficient that describes concentrations of both the dissolved and adsorbed solutes relative to a unit volume or mass of water.

The retardation factor then is defined by the equation

$$R_F = 1 + K_r \quad (4.4)$$

Using  $K_r$  as defined in equation 4.3, and  $R_F$  as defined in equation 4.4 has at least two advantages. First, most geochemical speciation codes express concentrations of adsorbed solutes in the same units as those used for dissolved solutes and therefore the simulation results can easily be used to define a  $K_r$  or  $R_F$  value. Second, it is very simple to convert between  $K_r$  values and the corresponding  $R_F$  values.

As discussed in chapter 2, a significant limitation of the  $K_d$  approach is that it does not account for the possible variable chemical conditions in the subsurface or for the possibly limited number of sorption sites. The surface complexation model (SCM) is one approach that can account for these effects. In this approach, the adsorbing surface is considered to possess surface functional groups that can form surface complexes analogous to the formation of aqueous complexes with ligands in solution (Stumm and Morgan, 1996). The adsorption interaction is written as a balanced chemical reaction and is described by a mass action expression (equilibrium equation) that is sometimes corrected for electrical double-layer effects (Stumm and Morgan, 1981; Dzombak and Morel, 1990). Figure 4.1 illustrates a simplified SCM for the adsorption

of U(VI) ( $\text{UO}_2^{+2}$ ). In this model,  $\text{UO}_2^{+2}$  can react with surface sites to form a surface complex ( $\text{SOUO}_2\text{OH}$ ) or  $\text{UO}_2^{+2}$  can react with a ligand ( $\text{L}^-$ ) to form an aqueous complex ( $\text{UO}_2\text{L}_3^{2-3n}$ ). If electrostatic effects and activity corrections are ignored, the equilibrium equation for the formation of the surface complex is:

$$K_S = \frac{(>\text{SOUO}_2\text{OH})(\text{H}^+)^2}{(>\text{SOH})(\text{UO}_2^{+2})} \quad (4.5)$$

where the quantities in parentheses are concentrations of dissolved or adsorbed solutes in units of mol/L (or kg) of water and the activity of water is assumed to equal 1.

$K_r$  for the simplified SCM illustrated in figure 4-1 can be defined by assuming that (1) the surface site density ( $S_T$ ) is constant and equal to the sum of  $>\text{SOH}$  and  $>\text{SOUO}_2\text{OH}$ , (2) the concentration of the ligand is constant (a good approximation for the complexation of trace concentrations of an actinide by carbonate in the presence of calcite), and (3) the concentration of the aqueous complex  $\text{UO}_2\text{L}_3^{2-3n}$  equals  $K_L(\text{UO}_2^{+2})(\text{L})^3$ . With these assumptions,  $K_r$  can be defined by:

$$K_r = \frac{K_S S_T}{[K_S(\text{UO}_2^{+2})^2 + (\text{H}^+)^2] + [1 + K_L(\text{L})^3]} \quad (4.6)$$

Although equation 4.6 does not replace the need to model speciation by using a general-purpose geochemical simulator, it can be used to illustrate the effects of speciation on  $K_r$  in certain simplified cases. Equation 4.6 shows that  $K_r$  is a nonlinear function of  $K_S$ ,  $\text{UO}_2^{+2}$ ,  $\text{H}^+$ , and  $\text{L}^-$  and a linear function of  $S_T$ . The bracketed term on the left side of the denominator illustrates the competition between  $\text{UO}_2^{+2}$  and  $\text{H}^+$  for the limited number of surface sites. The bracketed term on the right side of the denominator accounts for the distribution of U(VI) between the free ( $\text{UO}_2^{+2}$ ) and the complexed species ( $\text{UO}_2\text{L}_3^{2-3n}$ ).

Figure 4-2 illustrates the dependence of  $K_r$  on total  $\text{UO}_2^{+2}$  concentration, pH, and the L concentration for three pairs of  $K_S$  and  $S_T$  values. These pairs of values were selected to represent adsorption on a solid having a few strongly adsorbing sites, a solid having many weakly adsorbing sites, and an intermediate case. The solution conditions, except as modified for each plot, are pH = 7, total uranium ( $(\text{UO}_2^{+2})_T$ ) =  $10^{-7}$ ,  $\text{L} = 10^{-6}$ , and  $K_L = 10^{18}$ . Figure 4-2a illustrates that at small  $\text{UO}_2^{+2}$  concentrations,  $K_r$  is independent of  $\text{UO}_2^{+2}$  and that  $K_r$  decreases with increasing  $(\text{UO}_2^{+2})_T$  concentration. This change results because at small  $(\text{UO}_2^{+2})_T$  concentrations,  $K_S(\text{UO}_2^{+2})$  is much greater than  $(\text{H}^+)^2$  and at large  $\text{UO}_2^{+2}$  concentrations,  $K_S(\text{UO}_2^{+2})$  is much greater than  $(\text{H}^+)^2$ . At larger  $\text{UO}_2^{+2}$  concentrations, the  $K_S(\text{UO}_2^{+2})$  term domi-



nates and  $K_r$  is inversely proportional to  $\text{UO}_2^{+2}$ . Figure 4-2b illustrates that  $\log K_r$  increases in proportion to the pH until a plateau is reached that is dependent on the values of  $K_S$  and  $S_T$ . Again, this change results from the relative importance of the term  $K_S(\text{UO}_2^{+2})$  versus  $(\text{H}^+)^2$  in the denominator of equation 4.6. Finally, figure 4-2c illustrates that  $K_r$  decreases rapidly when the concentration of ligand is larger than approximately  $10^{-6}$  mol. At this concentration, and when the selected value of  $\log K_L$  equals 18, the value of  $K_L L^3$  starts to exceed unity and  $K_r$  decreases as the ligands in solution out-compete the surface for the  $\text{UO}_2^{+2}$ .

These effects on  $K_r$  of  $\text{UO}_2^{+2}$  concentration, pH, and ligand concentration recently have been demonstrated in a study of  $\text{UO}_2^{+2}$  transport in columns packed with quartz (Kohler and others, 1996). In that study, the retardation factor changed by a factor of 3 in response to (1) a pH change of 0.3 pH units, (2) a change in  $\text{UO}_2^{+2}$  concentration by a factor of 50, or (3) the addition of 0.1 mM of fluoride, a moderately strong complexing ligand for  $\text{UO}_2^{+2}$ .

In the following sections, the results of speciation calculations for Am, U, Np, and Pu are presented to illustrate the potential variability in adsorption properties of ground waters at the INEEL.

### 4.3.1 Am, U, Np, and Pu chemistry and speciation

#### 4.3.1.1 Am

In ground water, Am exists only as the trivalent  $\text{Am}^{+3}$  ion.  $\text{Am}^{+3}$  hydrolyzes to form  $\text{AmOH}^{+2}$ ,  $\text{Am}(\text{OH})_2^+$ , and  $\text{Am}(\text{OH})_3$ ; in the presence of  $\text{CO}_3^{-2}$ , the species  $\text{AmCO}_3^+$ ,  $\text{Am}(\text{CO}_3)_2^-$  and  $\text{Am}(\text{CO}_3)_3^{-3}$  also form. Silva and others (1995) evaluated thermodynamic data for the formation of these species, and complexes of Am(III) with  $\text{F}^-$ ,  $\text{SO}_4^{-2}$ , and  $\text{PO}_4^{-3}$ . These thermodynamic data were used in the calculations listed below. Although the existence of Am(III)- $\text{HCO}_3$  complexes have been suggested in the literature, Silva and others (1995) discounted their existence.

Figure 4-3 shows the computed distribution of aqueous Am(III) species for variable Am(III) concentrations and  $P_{\text{CO}_2}$  at different pH values. As in the speciation of other actinides, the hydrolysis species are more important at lower pH and  $P_{\text{CO}_2}$  values. The extent of hydrolysis increases with increasing pH, and at pH values above 7, Am- $\text{CO}_3$  complexes are the dominant aqueous species as shown in figure 4-3a for  $10^{-7}$  M Am and  $10^{-3.5}$  atm  $\text{CO}_2$ . At a larger Am(III) concentration ( $10^{-5}$  M) and  $10^{-3.5}$  atm  $\text{CO}_2$ , the distribution of species is almost identical to that for  $10^{-7}$  M Am(III) because no polynuclear Am(III) species are formed at the larger Am(III) concentration. Am-

$\text{CO}_3$  species are still dominant at pH values above 7. At  $10^{-2.5}$  atm  $\text{CO}_2$  and pH values above 6.5, the Am- $\text{CO}_3$  complexes become the dominant species.

Data from two studies (Righetto and others, 1988; Moulin and others, 1992) of the adsorption of  $\text{Am}^{+3}$  by single mineral phases were fitted to a diffuse double layer SCM by Turner (1995). The phases were quartz,  $\alpha$ -alumina, and  $\gamma$ -alumina.  $K_r$  values were calculated using the SCM parameters reported by Turner (1995) for a pH range from 4 to 10 and  $P_{\text{CO}_2}$  equal to  $10^{-3.5}$  and  $10^{-2.5}$  atm. The results of these calculations are shown in figure 4-4. The  $K_r$  values are smallest at low and high pH values, and largest at almost neutral pH values. The range of  $K_r$  values for the sorption of Am is very large. For the two different forms of aluminum oxide, the  $K_r$  values differ by three orders of magnitude. This difference is probably the result of the limited amount of adsorption data available (only one Am(III) concentration and one sorbent concentration were available for each solid) and the differences in solid properties. The  $K_r$  for sorption by quartz is smaller than that for  $\gamma$ -alumina by another three orders of magnitude.

#### 4.3.1.2 U

In subsurface environments, U exists primarily in either the +4 oxidation state, U(IV), or the +6 oxidation state, U(VI). Because minerals containing U(IV) are generally insoluble, most studies of U mobility in the subsurface consider only the U(VI) form. The U(VI) cation is coordinated axially by two oxygen atoms. This arrangement creates a linear species with a nominal charge of +2, typically called  $\text{UO}_2^{+2}$ , which reacts to form many different aqueous species in natural water. Because U(VI) mobility is dependent on the competition between aqueous ligands and surface ligands, it is worthwhile to consider the types and predominance of the different aqueous species. Grenthe and others (1992) summarized thermodynamic data for U(VI) speciation reactions with many ions including  $\text{OH}^-$ ,  $\text{CO}_3^{-2}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{F}^-$ ,  $\text{PO}_4^{-3}$ . Although the data in Grenthe and others (1992) were critically evaluated by an international committee assembled by the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD), use of the data could be limited because of the lack of data for some species. For example, Grenthe and others (1992) acknowledged that there are no thermodynamic data for the formation of U orthosilicate ( $\text{UO}_2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , soddyite), even though x-Ray diffraction studies previously had demonstrated that this solid exists. A second example of the limitations of the data base in Grenthe and others (1992) is that, although synthetic organic chelating agents such as ethylenediaminetetraacetic acid (EDTA) and nat-

#### 4-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

ural organic matter are known to form strong to moderately strong complexes with U(VI) (Choppin and Allard, 1985), neither of these nor any other organic species are included. In spite of these limitations and others (for example, slow kinetics), it is instructive to use the available data to consider the aqueous complexes that could form.

In natural water, U(VI) hydrolyzes to form multiple hydrolysis species that can be either mononuclear (for example  $\text{UO}_2\text{OH}^+$ ,  $\text{UO}_2\text{OH}_2^0$ , etc.) or, at large concentrations, polynuclear (for example  $(\text{UO}_2)_3(\text{OH})^{5+}$ ,  $(\text{UO}_2)_3(\text{OH})_4^{+2}$ , etc.). U(VI) also reacts with carbonate ions in solution to form the U carbonate complexes  $\text{UO}_2\text{CO}_3$ ,  $\text{UO}_2(\text{CO}_3)_2^{-2}$ , and  $\text{UO}_2(\text{CO}_3)_3^{-4}$ . In addition to these complexes, several U hydroxy-carbonate species also can form. The formation of hydroxy and carbonate complexes of U(VI) in natural water indicates that both the pH and the  $P_{\text{CO}_2}$  are variables that control U(VI) speciation in ground water. Figure 4-5 illustrates the results of speciation calculations for variable U(VI) concentrations and  $P_{\text{CO}_2}$  at different pH values. At  $10^{-7}$  M U(VI) and atmospheric  $P_{\text{CO}_2}$ , the mononuclear species are the dominant forms of U(VI) in the system, although the number of coordinating ligands increases as pH increases. As pH increases, the dominant form of U(VI) changes to  $\text{UO}_2\text{OH}^+$  at a pH of 5.5 and to  $\text{UO}_2(\text{OH})_2^0$  at a pH of 6.3 (fig. 4-5a). When pH is higher than 7.2, U(VI) -  $\text{CO}_3^{-2}$  complexes are the dominant species. At larger U(VI) concentration ( $10^{-5}$  M) and at atmospheric  $P_{\text{CO}_2}$ , polynuclear species are more important. In these conditions, when pH ranges from 5.8 to 8.5, the polynuclear species  $(\text{UO}_2)_3(\text{OH})_5^+$  and  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$  are the dominant species and above pH 8.5 the  $\text{UO}_2(\text{CO}_3)_3^{-4}$  complex is the dominant species. Finally, when  $P_{\text{CO}_2}$  is equal to  $10^{-2.5}$  atm, a value more representative of soil  $P_{\text{CO}_2}$  values and approximately equal to the upper limit of  $P_{\text{CO}_2}$  values at the SDA, the  $\text{UO}_2\text{-CO}_3$  complexes are the dominant species above pH 6 starting first with the monocarbonate complex followed by the dicarbonate and tricarboxate complexes (fig. 4-5c).

There have been several studies on the sorption of U(VI) in well-defined systems. These include studies of U(VI) adsorption on goethite (Tripathi, 1983), ferrihydrite (Hsi and Langmuir, 1985; Waite and others, 1994), montmorillonite (McKinley and others, 1995; Pabalan and others, 1997), quartz (Kohler and others, 1996), clinoptilolite (Pabalan and others, 1998), and alumina (Pabalan and others, 1998). At low pH values, U(VI) adsorption increases over a narrow pH range of approximately 1 to 2 pH units resulting in what is commonly called an adsorption edge. The pH of the adsorption edge

varies with the adsorbing mineral and the amount of available surface area but is generally between 4 and 5. In the absence of  $\text{CO}_2$  and at pH values up to approximately 9, U(VI) is essentially completely adsorbed by goethite (Hsi and Langmuir, 1985; Tripathi 1983).

In the presence of  $\text{CO}_2$ , the adsorption is more complex. The formation of  $\text{UO}_2(\text{CO}_3)_2^{-2}$  and  $\text{UO}_2(\text{CO}_3)_3^{-4}$  results in decreased adsorption at high pH values. The pH value at which sorption decreases varies as  $P_{\text{CO}_2}$  values and surface properties change. In the presence of atmospheric  $\text{CO}_2$  and when pH is higher than 8, practically no U(VI) is adsorbed by goethite (Hsi and Langmuir, 1985; Tripathi 1983) or ferrihydrite (Waite and others, 1994). Modeling studies have shown that the adsorbing species also may change in the presence of  $\text{CO}_2$ . It has been postulated (Hsi and Langmuir, 1985; Tripathi, 1983; Waite and others, 1994) that, in the presence of  $\text{CO}_2$ , ternary complexes involving a surface site, U(VI) and  $\text{CO}_3^{-2}$  may be significant, if not the most dominant surface species. These postulated surface species eventually were confirmed by spectroscopy (Waite and others, 1994). Thus, in the ferrihydrite and goethite systems, and perhaps in other systems,  $\text{CO}_3^{-2}$  complexation forms a stronger surface species than species formed in the absence of  $\text{CO}_3^{-2}$ , but the strength of this species is still insufficient to overcome the aqueous carbonate complexes, particularly  $\text{UO}_2(\text{CO}_3)_3^{-4}$ .

The surface complexation approach has been used in at least five studies to model U(VI) sorption by different mineral surfaces. Most of the data reported in these studies were fitted to the Diffuse Double Layer model (Dzombak and Morel, 1990) or the Triple Layer model (Davis and others, 1978). For this report, only results from the Diffuse Double Layer model were considered. In many instances the composition of the sorbed species is not directly known from spectroscopy which often leads to a trial-and-error approach to formulating the reactions in a surface complexation model. Zachara and others (1995) and McKinley and others (1995) inferred the surface species from aqueous speciation calculations and suggested that the surface species at the edge sites of clay minerals ( $>\text{XO}^-$ ) were  $>\text{XO-UO}_2^{2+}$  and  $>\text{XO-}(\text{UO}_2)_3(\text{OH})_5$ . This latter species contributes to the formation of a multinuclear species involving 3  $\text{UO}_2^{+2}$  ions. As in the case of solution speciation, the formation of this complex should depend on the total U(VI) concentration; however, multiple total U(VI) concentrations were not considered. Waite and others (1994) considered a range of U(VI) concentrations of four orders of magnitude and found that the U(VI) adsorption could be modeled by assuming that only mononuclear complexes adsorbed on ferrihydrite and that

two types of sites having different binding energies existed.

The reactions and the logarithms of the equilibrium constants ( $\log K$ ) for the five different SCM's are summarized in table 4-1.

The differences in the SCM's in table 4-1 illustrate several different approaches that have been used to model the sorption reactions. These differences are often the result of assuming that the sorbed species is related to the dominant aqueous species. Although this has worked well for modeling the sorption of transition metals by ferrihydrite (Dzombak and Morel, 1990), the greater complexity of the aqueous speciation of U(VI) solutions has led to these different modeling approaches. Waite and others (1994) used spectroscopic studies to evaluate the structure of the adsorbed U(VI) species. This independent surface information was used as a basis for writing the SCM reactions. The variety of approaches illustrated in table 4-1 indicates that surface complexation modeling of U(VI) is still an evolving process and that the optimal approach has not been determined.

Although application of SCM's is still an evolving process, it is useful to examine the  $K_r$  values for different chemical conditions. Figure 4-6 shows the  $K_r$  value for the SCM by Waite and others (1994) for a pH range from 4 to 10 and variable  $P_{CO_2}$  and sorption site density. For a system with a total adsorption site density of 1 millimole per liter of solution (1 mM) and at atmospheric  $P_{CO_2}$ , the  $K_r$  values range from less than 1 at pH values near 4 and above pH 8.6 to more than 1,000 at pH 7. If the  $P_{CO_2}$  is increased by a factor of ten to  $10^{-2.5}$  atm (which is still in the range of subsurface conditions at the SDA), the  $K_r$  values are significantly smaller at pH values above 7. Figure 4-6 also illustrates  $K_r$  values for a system with a  $P_{CO_2}$  of  $10^{-2.5}$  atm and total adsorption site density of 10 mM. For this system, sorption is increased relative to the system of 1 mM sites and atmospheric  $P_{CO_2}$  below pH 7.5 but sorption is smaller above this pH. Although the total sorption site density at the SDA is not well known, values in the range from 1 mM to 10 mM may be reasonable based on similar SCM studies at research sites near Bemidji, Minn. and Cape Cod, Mass. as discussed in section 4.3.2.

Figure 4-7 illustrates  $K_r$  values for four of the SCM's listed in table 4-1 for both atmospheric  $P_{CO_2}$  and  $10^{-2.5}$

atm  $CO_2$ . The four different SCM's illustrate generally similar behavior of  $K_r$  values in that the  $K_r$  values are small at both low and high pH values and are largest at almost neutral pH values; however, the range of  $K_r$  values for the different mineral surfaces is significant. The  $K_r$  values for quartz and montmorillonite are generally 1 to 2 orders of magnitude smaller than those for the iron-containing solids goethite and ferrihydrite. This discrepancy is greater at large  $P_{CO_2}$  values because the goethite and ferrihydrite SCM's account for the formation of the ternary  $UO_2^{+2}-CO_3^{-2}$  surface complex, which counteracts, to a limited extent, the tendency to form aqueous species  $UO_2(CO_3)_3^{-4}$ . In the system with  $10^{-2.5}$  atm  $CO_2$ , the  $K_r$  values are smaller than 30 at pH 8, which indicates that U(VI) may be mobile in these conditions which are present in some parts the subsurface at the SDA.

#### 4.3.1.3 Np

In most ground-water environments, the dominant oxidation states of Np are Np(IV) and Np(V). The aqueous stability field of Np(V) is particularly large. In oxidizing environments, such as those at the INEEL, Np(V) is the dominant oxidation state and  $NpO_2^{+}$  probably is the dominant aqueous species.

Sorption behavior of Np(V) on quartz, clinoptilolite, montmorillonite and  $\alpha$ -alumina generally is similar (Bertetti and others, 1998). Sorption of Np(V) increases with increasing pH up to a pH of 8 to 8.5, at which point sorption may decrease. If the  $CO_2$  concentration in ground waters is in equilibrium with atmospheric  $CO_2$ , the increased formation of aqueous Np(V) carbonate complexes inhibits the sorption of Np(V). The dependence of Np(V) sorption on pH results in a change of about one order of magnitude in the effective  $K_d$  values for a change of 1 to 2 pH units in a given experiment.

Surface complexation data for conditions in which  $P_{CO_2}$  values are larger than atmospheric are sparse. Generally, soil  $P_{CO_2}$  values can be expected to exceed atmospheric  $P_{CO_2}$  values by about 2 orders of magnitude. When  $P_{CO_2}$  values are large, Np hydroxy-carbonate surface complexes could possibly be important, given that such complexes have been found important U(VI) sorption on ferrihydrite (Waite and others, 1994).

#### 4-6 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 4-1. Surface complexation models for describing the adsorption of U(VI) by selected mineral surfaces

[Log K, logarithm of the equilibrium constant; References: A = Pabalan and others, 1998; B = Payne and others, 1992; C = Pabalan and Turner, 1996; D = Turner, 1995; E = Waite and others, 1994]

Mineral surface	Reaction	Log K	Reference
Quartz	$\text{SiOH} = \text{SiO}^- + \text{H}^+$	-7.20	A
	$\text{SiOH} + \text{UO}_2^{+2} = \text{SiOUO}_2^{+2} + \text{H}^+$	0.3	
	$\text{SiOH} + \text{UO}_2^{+2} + \text{H}_2\text{O} = \text{SiOUO}_2\text{OH} + 2\text{H}^+$	-5.65	
	$\text{SiOH} + 3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = \text{SiO}(\text{UO}_2)_3(\text{OH})_5 + 6\text{H}^+$	-16.75	
Kaolinite	$\text{SiOH} = \text{SiO}^- + \text{H}^+$	-7.2	B
	$\text{SiOH} + \text{UO}_2^{+2} = \text{SiOUO}_2^+ + \text{H}^+$	0.96	
	$\text{SiOH} + \text{UO}_2^{+2} = \text{SiOUO}_2^{-2}$	5.73	
	$\text{SiOH} + \text{UO}_2^{+2} + \text{H}_2\text{O} = \text{SiUO}_2\text{OH} + 2\text{H}^+$	-5.84	
	$\text{AlOH} + \text{H}^+ = \text{AlOH}_2^+$	8.33	
	$\text{AlOH} = \text{AlO}^- + \text{H}^+$	-9.73	
	$\text{AlOH} + \text{UO}_2^{+2} = \text{AlOUO}_2^+ + \text{H}^+$	2.18	
	$\text{AlOH} + \text{UO}_2^{+2} = \text{AlOHUO}_2^{+2} + \text{H}^+$	9.20	
	$\text{AlOH} + \text{UO}_2^{+2} + \text{H}_2\text{O} = \text{AlUO}_2\text{OH} + 2\text{H}^+$	-4.74	
Montmorillonite	$\text{SiOH} = \text{SiO}^- + \text{H}^+$	-7.20	C
	$\text{SiOH} + \text{UO}_2^{+2} = \text{SiOUO}_2^{+2} + \text{H}^+$	2.6	
	$\text{SiOH} + 3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = \text{SiO}(\text{UO}_2)_3(\text{OH})_5 + 6\text{H}^+$	-15.29	
	$\text{AlOH} + \text{H}^+ = \text{AlOH}_2^+$	8.33	
	$\text{AlOH} = \text{AlO}^- + \text{H}^+$	-9.73	
	$\text{AlOH} + \text{UO}_2^{+2} = \text{AlOUO}_2^+ + \text{H}^+$	2.7	
	$\text{AlOH} + 3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = \text{Al}(\text{UO}_2)_3(\text{OH})_5 + 6\text{H}^+$	14.95	
Goethite	$\text{FeOH} + \text{H}^+ = \text{FeOH}_2^+$	6.47	D
	$\text{FeOH} = \text{FeO}^- + \text{H}^+$	-9.03	
	$\text{FeOH} + \text{UO}_2^{+2} + \text{CO}_3^{-2} + \text{H}^+ = \text{FeOHUO}_2\text{CO}_3\text{H}^+$	17.43	
Ferrihydrite	$\text{FeOH} + \text{H}^+ = \text{FeOH}_2^+$	6.51	E
	$\text{FeOH} = \text{FeO}^- + \text{H}^+$	-9.13	
	$\text{FeOH} + \text{H}_2\text{CO}_3 = \text{FeCO}_3\text{H} + \text{H}_2\text{O}$	2.90	
	$\text{FeOH} + \text{H}_2\text{CO}_3 = \text{FeCO}_3^- + \text{H}_2\text{O} + \text{H}^+$	-5.09	
	$(\text{Fe}_s(\text{OH})_2) + \text{UO}_2^{+2} = (\text{Fe}_s\text{O}_2)\text{UO}_2 + 2\text{H}^+$	-2.57	
	$(\text{Fe}_w(\text{OH})_2) + \text{UO}_2^{+2} = (\text{Fe}_w\text{O}_2)\text{UO}_2 + 2\text{H}^+$	-6.28	
	$(\text{Fe}_s(\text{OH})_2) + \text{UO}_2^{+2} + \text{CO}_3^{-2} = (\text{Fe}_s\text{O}_2)\text{UO}_2\text{CO}_3^{-2} + 2\text{H}^+$	3.67	
	$(\text{Fe}_w(\text{OH})_2) + \text{UO}_2^{+2} + \text{CO}_3^{-2} = (\text{Fe}_w\text{O}_2)\text{UO}_2\text{CO}_3^{-2} + 2\text{H}^+$	-0.42	

## 4.3.1.4 Pu

Cleveland (1979) and Carnall and Choppin (1983) discussed the chemical behavior of Pu in natural environments and in laboratory experiments. The results presented in these references, particularly in Cleveland's compilation of Pu data (Cleveland, 1979), indicate that there are many uncertainties in attempting to predict, or even to describe, the chemical behavior of Pu in ground-water environments. Although a large amount of thermodynamic data for Pu have been collected, and several thermodynamic data bases are currently available (the HATCHES and EQ3/6 data bases), there are many uncertainties regarding the accuracy and consistency of these data. For example, most Pu speciation constants have been determined by using acidic solutions of HCl, HClO<sub>4</sub>, or HNO<sub>3</sub>. Use of acidic solution raises some troubling questions: How valid are these speciation constants? How valid is the Pu aqueous thermodynamic model when higher pH values are used, such as those between 8 and 8.5 that are generally found in ground water at the INEEL? Have all the relevant speciation and complexation reactions that are likely to predominate when pH values are high been documented and appropriately determined? The problems posed by Pu(IV) hydrolysis and Pu(OH)<sub>x</sub> polymerization as pH values are increased indicate why most complexation and speciation reactions, especially for Pu(IV) species for conditions in which pH values are low, have been studied. The formation of Pu(IV) hydroxide polymers is well documented in the literature, and yet the conditions that cause the polymers to be in colloidal form or to precipitate out of solution and the conditions that cause depolymerization are not well known. The polymerization reaction is not accounted for in either the EQ3/6 (Wolery, 1992a, 1992b; Wolery and Daveler, 1992) or HATCHES (Cross and Ewart, 1991) thermodynamic data bases. Even if thermodynamic data were available, their usefulness could be limited by the relatively slow kinetics of polymerization, especially depolymerization. The question of colloid stability also would arise.

Although the complexation behavior of Pu with commonly used laboratory chelates such as EDTA is relatively well understood, the complexation behavior of Pu in contact with natural organic matter in both dissolved and solid forms is not well understood. Preliminary indications are that, in waters from granitic or sedimentary formations, organic complexes probably dominate the speciation of trivalent actinides (such as Am<sup>3+</sup>) and that inorganic complexes (such as hydroxide or carbonate species) probably dominate the speciation of pentavalent and hexavalent actinides (Np, U, Pu) (Moulin and others,

1992). Of course, in ground water having large concentrations of organic carbon (dissolved or solid), high oxidation states of actinides eventually may be reduced to trivalent or tetravalent oxidation states by oxidation of the organic carbon.

The oxidation state of actinide ions strongly determines their chemical interactions. In general, actinides in trivalent, tetravalent and hexavalent states are strongly complexed by carbonate, humate, and hydroxide ligands, moderately complexed by SO<sub>4</sub> and F, and weakly complexed by Cl (Jensen and others, 1996). Actinides in the pentavalent state, such as Np and Pu, however, show considerable aqueous stability even in the absence of complexing anions such as carbonate (Jensen and others, 1996).

Although Pu K<sub>d</sub>s, that is, the distribution of gross Pu between aqueous and solid phases (generally crushed in the case of hard rocks or consolidated materials), have been measured during numerous experiments, relatively few specific surface complexation and ion exchange constants from these experiments have been determined. Although K<sub>d</sub>s can be useful practical indicators of radionuclide sorptive affinity, the K<sub>d</sub> measurements themselves often are made with little attention to the chemical processes responsible for the distribution. The results are generally applicable only to the specific conditions under which the experiments were carried out and, consequently, may be difficult to use in the prediction of radionuclide transport (see section 5.2.1).

Finally, it must be acknowledged that, although a high-quality thermodynamic data base capable of fully describing the aqueous speciation of Pu and its potential sorption and precipitation/dissolution reactions would be useful, such a data base still would not necessarily be able to predict the behavior of Pu in the ground-water environment. Indeed, many reactions may be limited kinetically and, therefore, a thermodynamic description would be of limited use. Predicting the transport behavior of Pu is also difficult because of the complexity and chemical and physical heterogeneity of natural ground water. The variability of the redox environment and the redox sensitivity of Pu make accurate transport predictions particularly difficult.

In most ground water, Pu exists in more than one oxidation state. In reducing environments, Pu(III) and Pu(IV) are the dominant oxidation states. In oxidizing environments, such as those at the INEEL, Pu(IV), Pu(V), and possibly Pu(VI) are the dominant oxidation states. Unless F, P, and SO<sub>4</sub> concentrations are very large, oxide, hydroxide, and carbonate complexes of Pu can be expected to be the dominant species.

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Pu(V) and Pu(IV) sorption on  $\gamma$ -alumina and goethite generally increases as a function of pH (Turner, 1995); however, Pu(IV) sorption on goethite occurs at pH values between 2 and 6, whereas Pu(V) sorption on goethite occurs at pH values between 4 and 8. Pu(V) sorption on  $\gamma$ -alumina also occurs at pH values between 6 and 10. In contrast, Pu sorption on amorphous silica or on quartz is expected to occur at much lower pH values because of the much lower  $pH_{ZPC}$  (the pH point of zero charge), near 2, of these materials compared with that of the iron and aluminum oxyhydroxides, which generally occurs between 7 and 9.

Because U(VI)-carbonate complexes, which are similar to Pu-carbonate complexes, generally sorb and form surface complexes, Pu carbonate complexes also may sorb and form surface complexes; however, there is no current (1999) information on the possible formation of these complexes.

### 4.3.2 Speciation calculations for aqueous Am, U, Np, and Pu in INEEL waters

#### 4.3.2.1 Speciation calculations for aqueous Am

In spite of the large range of  $K_r$ s calculated for the reported SCM's for Am(III) (see section 4.3.1.1), speciation of Am(III) in each of the water samples listed in table

4-4 (see discussion under speciation calculation for aqueous Np and Pu, section 4.3.2.3) was calculated. The results are shown in table 4-2. The  $K_r$ s of the different sorbing phases in water samples from each sampling site varied by more than 4 orders of magnitude. The  $K_r$  values of quartz and  $\gamma$ -alumina in all ground-water samples varied by approximately a factor of 6; the  $K_r$ s of  $\alpha$ -alumina were almost invariant.

For the case of Am, the SCM's derived from laboratory studies illustrate the large uncertainty in assessing the potential for mobility below the SDA because of the wide variability in the computed  $K_r$ s.

#### 4.3.2.2 Speciation calculations for aqueous U

The speciation of U(VI) in each of the water samples listed in table 4-3 was calculated and  $K_r$  values were computed. The calculations included adsorption by quartz, montmorillonite, goethite, and ferrihydrite and assumed a surface site concentration of 1 mM. In addition, one set of calculations for sorption by ferrihydrite assumed a surface site concentrations equal to 10 mM. The results, summarized in table 4-3, indicate that small  $K_r$ s were expected if quartz and montmorillonite were the sorbing phases at surface site concentrations of 1 mM. The  $K_r$  values calculated for the ground-water samples ranged from 7 to 211 for goethite and from 2 to 41 for ferrihydrite. Generally, the  $K_r$  values decreased as pH and  $P_{CO_2}$  values

Table 4-2. Computed Am  $K_r$  values of five surface complexation models for water samples from the Idaho National Engineering and Environmental Laboratory

[mM, millimoles per liter]

Sampling site	pH	$P_{CO_2}$	Quartz	$\gamma$ -Alumina	$\alpha$ -Alumina
			1 mM sites	1mM sites	1mM sites
Big Lost River below INEEL diversion	6.4	-1.08	3E+01	2E+05	7E+07
USGS 92	8.4	-3.03	2E+03	3E+06	9E+07
EBR 1	8.2	-3.1	3E+03	5E+06	9E+07
NPR Test	8.0	-2.76	2E+03	3E+06	9E+07
P&W 2	8.0	-2.86	2E+03	4E+06	9E+07
USGS 8	8.1	-2.92	2E+03	3E+06	9E+07
USGS 19	7.8	-2.53	9E+02	2E+06	8E+07
USGS 112	7.8	-2.74	2E+03	3E+06	9E+07
RWMC Production	8.1	-2.93	2E+03	4E+06	9E+07
USGS 87	8.1	-3.05	3E+03	5E+06	9E+07
USGS 89	8.3	-3.38	6E+03	8E+06	9E+07
USGS 90	8.1	-3.02	3E+03	5E+06	9E+07

Table 4-3. Computed  $U K_r$  values of five surface complexation models for water samples from the Idaho National Engineering and Environmental Laboratory

[mM, millimoles per liter]

Sampling site	pH	$P_{CO_2}$	Quartz	Montmorillonite	Goethite	Ferrihydrite	Ferrihydrite
			1 mM sites	1 mM sites	1 mM sites	1 mM sites	10 mM sites
Big Lost River below INEEL diversion	6.4	-1.08	5	1.2	6,119	128	1402
USGS 92	8.39	-3.03	0.1	0.03	7	2	19
EBR 1	8.2	-3.1	1	0.3	41	10	110
NPR Test	8.0	-2.76	0.7	0.2	55	11	121
P&W 2	8.0	-2.86	1.5	0.8	93	20	216
USGS8	8.1	-2.92	0.6	0.2	40	9	96
USGS 19	7.8	-2.53	0.7	0.2	98	18	190
USGS 112	7.8	-2.74	2.6	0.8	211	41	442
RWMC Production	8.1	-2.93	0.9	0.3	52	12	127
USGS 87	8.1	-3.05	1.8	0.6	80	19	206
USGS 89	8.3	-3.38	2.9	1	62	19	210
USGS 90	8.1	-3.02	1.6	0.5	72	17	183

increased.  $K_r$  values generally increased in proportion to the number of adsorbing sites when ferrihydrite was the sorbing phase and the surface site concentration was 10 mM. The  $K_r$ s of each sorbing phase in the SCM's varied by a factor of 20 to 30 for ground-water samples. The dominant U(VI) species in all of the surface- and ground-water samples were the carbonate complexes  $UO_2(CO_3)_3^{4-}$  and  $UO_2(CO_3)_2^{2-}$ ; complexes with other anions ( $OH^-$ ,  $SO_4^{2-}$ ,  $F^-$ ,  $NO_3^-$  and  $PO_4^{3-}$ ) were insignificant because of small anion concentrations or small formation constants. While it may be difficult to extrapolate the results shown in table 4-3, they indicate that U(VI) may be mobile because of the formation of soluble U(VI) carbonate complexes and the values of pH and  $P_{CO_2}$  and the nature of the sorbing site that are important in controlling the mobility of U(VI). The potential mobility of U(VI) is particularly notable for the perched water from well USGS 92.

#### 4.3.2.3 Speciation calculations for aqueous Np and Pu

Thermodynamic data for aqueous Np and Pu were obtained from the ANSTO thermodynamic data base (Marianne Guerin, written commun., 1998), which was derived from the HATCHES data base (Cross and Ewart,

1991)<sup>2</sup>. Because the database contains enthalpy data only for the major Pu species, the temperature dependence of Np and Pu speciation at temperatures other than 25°C could not be properly modeled. Surface complexation constants fitted to the Diffuse Double Layer SCM (Dzombak and Morel, 1990) were obtained from Turner (1995) for Pu(IV), Pu(V), and Np(V) sorption by goethite. Some surface complexation data for sorption of Np(V) (mainly) and Pu(V) (occasionally) on other phases, such as  $\gamma$ -alumina,  $\alpha$ -alumina, boehmite ( $\gamma$ -AlOOH), lepidocrocite ( $\gamma$ -FeOOH), ferrihydrite, amorphous-silica, montmorillonite and kaolinite (Turner, 1995; Turner and others, 1998) were also available, but these data were not used in the initial examples presented here. The Np and Pu aqueous complexation and surface complexation constants were added to the default data base in the USGS geochemical computer code PHREEQC version 2 (Parkhurst and Appelo, 1999). Ideally, all thermodynamic data within a

<sup>2</sup>The Np and Pu data in the ANSTO (Australian Nuclear Science and Technology Organization) data base were checked and found to be identical to Np and Pu data in the HATCHES data base. Np and Pu data in both data bases were converted to PHREEQC format by Pierre Glynn and Robert Greene of the USGS.

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data base is internally consistent. This usually is not the case even for well-established data bases and certainly is not the case for the composite data base that was assembled for these calculations. Consequently, the calculations presented for Np and Pu in surface and ground water at the INEEL should be considered only generally illustrative of Np and Pu behavior in aqueous environments.

The geochemical speciation of Np and Pu in water samples from within or near the INEEL having a wide range of chemical compositions was simulated by using the PHREEQC code and the ANSTO thermodynamic data base amended with the SCM's from Turner (1995). For all simulations,  $10^{-8}$  mol/kg of water of Np and Pu also were assumed to be present. All water samples were oxygenated and primarily  $\text{CaHCO}_3$  types, although Ca:Na ratios, pH values, alkalinities, and DO concentrations varied significantly. All samples, except those from the Big Lost River (BLR) below the INEEL diversion (fig. 2-3), were ground-water samples. Water from well USGS 112 (fig. 2-3) was rich in Cl and represents water from the SRP aquifer taken from contamination plumes down gradient from the Idaho Nuclear Technology and Engineering Center (INTEC, formerly the Idaho Chemical Processing Plant). Well EBR-1, which is directly up gradient from the SDA (figure 2-2), represents deeper Snake River Plain (SRP) aquifer water. Well NPR Test, which is up gradient from the SDA, represents water from outside areas of known contaminant plumes. Water from well P&W2 (figure 2-3) represents underflow from the Birch Creek drainage. Water from well USGS 8 (figure 2-3) represents underflow from the BLR drainage. Water from well USGS 19 (figure 2-3) represents underflow from the Little Lost River drainage. Water from well USGS 92 (figure 2-3) represents perched water above the C-D interbed at the SDA. Water from wells RWMC Production, USGS 87, USGS 89, and USGS 90 (figure 2-3) represent water from the SDA area. Chemical compositions of water speciated with the PHREEQC model are shown in table 4-4.

PHREEQC was used to calculate the aqueous speciation of Np and Pu in the water samples listed above, and to calculate the speciation of goethite surfaces in equilibrium with the specified aqueous compositions. The goethite surface was assumed to contain  $5 \times 10^{-6}$  mol of surface sites per kg of  $\text{H}_2\text{O}$  and to have a surface area of  $54 \text{ m}^2/\text{kg}$  of water. Only surface complexes of Np(V), Pu(IV), and

Pu(V), and protonated, deprotonated and neutral surface hydroxyl sites were considered in the calculations. Surface complexation of Np(VI) and Pu(VI) and of major ions, such as Ca, Mg,  $\text{SO}_4$ , and  $\text{CO}_3$ , were not considered because of a lack of data about their surface complexation with goethite. Redox equilibrium with the DO concentrations measured in the water samples was assumed and the redox state of the solutions and the corresponding distribution of heterovalent Pu and Np species were determined. The surface complexation reactions, the Np aqueous complexation reactions, and most of the Pu aqueous complexation reactions (except notably that of the  $\text{PuO}_2(\text{CO}_3)_2^{-2}$  species) were assumed to be temperature independent, because of a lack of enthalpy data for these reactions. Temperature dependence was accounted for, however, in the speciation of major constituents.

Significant results of the PHREEQC speciation calculations are given in tables 4-5, 4-6, and 4-7. Although not shown in the tables, most of the water samples were almost saturated, or slightly supersaturated with respect to calcite. The calculated equilibrium partial pressures of  $\text{CO}_2$  and  $\text{O}_2$  show that most of the water samples were slightly supersaturated with respect to atmospheric oxygen and supersaturated with respect to atmospheric  $\text{CO}_2$  by approximately a factor of 3. In addition to giving the most significant surface complex species for Np and Pu and their concentrations, table 4-5 also gives  $K_r$  values, that is the calculated molar ratios of total sorbed Np (or Pu) to total aqueous Np (or Pu).

The PHREEQC speciation calculations show that Np(V) was the dominant redox state for aqueous Np speciation in the INEEL water samples. The Np(VI) concentrations are also significant, and are the dominant redox state in the perched-water sample. Np(IV) and Np(III) concentrations were insignificant. The neptunyl ion,  $\text{NpO}_2^+$ , is generally the dominant aqueous species, but Np(V) and Np(VI) neptunyl carbonate species,  $\text{NpO}_2\text{CO}_3^-$ ,  $\text{NpO}_2(\text{CO}_3)_2^{-2}$ , and  $\text{NpO}_2(\text{CO}_3)_3^{-4}$  were also important.

The calculations also show that Pu(V) was the dominant redox state for the INEEL water samples and  $\text{PuO}_2\text{CO}_3^-$  was the overwhelmingly dominant aqueous Pu species. Pu(IV) and Pu(VI) species concentrations were relatively small, except in the water sample from the BLR, which had a much lower pH.



Table 4-4. Chemical compositions of water speciated with the PHREEQC model

[Temperature, in degrees Celsius. Concentrations are in milligrams per liter. Abbreviations: DO = dissolved oxygen. Alk = alkalinity. \*the water assumed to be at equilibrium with atmospheric O<sub>2</sub>. Alkalinity expressed as CaCO<sub>3</sub>, except for the Big Lost River sample, \*\*, which is expressed as HCO<sub>3</sub>]

Sampling site	Temperature	pH	DO	Ca	Mg	Na	K	SiO <sub>2</sub>	Alk.	Cl	SO <sub>4</sub>	F	NO <sub>3</sub> <sup>as</sup> N	P
Big Lost River below INEEL diversion	10	6.4	8.24*	61	18	11	1.7	15	260**	8.2	23	0.3	NA	
Perched water USGS 92	13.5	8.39	7.91*	29	17	120	12	22	238	81	64	.4	NA	0.18
EBR 1	19.5	8.2	6.7	24	16	9.0	3.4	34	116	7.4	13	.2	.39	
NPR Test	14.5	8.0	9.2	59	15	8.4	2.5	22	173	20	26	.2	1.1	
P&W 2	10.5	8.0	9.7	40	14	7.9	1.2	14	139	11	21	.3	.38	
USGS 8	12	8.1	8.0	46	15	6.7	1.8	20	154	10	22	.3	.86	
USGS 19	17.5	7.8	6.9	48	18	13	1.6	16	177	14	24	.3	1.1	
USGS 112	14	7.8	6.6	70	18	47	4.5	23	116	120	34	.3	3.8	
RWMC Production	13	8.1	8.2	45	15	9.0	2.8	28	148	13	27	.2	.67	.03
USGS 87	14	8.1	10.2	40	14	12	3.0	28	111	13	26	.2	.68	
USGS 89	14	8.3	11.6	26	16	20	3.9	30	82	38	36	.3	1.8	
USGS 90	13.5	8.1	9.6	44	15	9.4	2.7	27	120	13	27	.2	.69	

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Table 4-5. Calculated partial pressures of CO<sub>2</sub> and O<sub>2</sub> and redox state distributions of aqueous Np and Pu in water samples from sites at or near the Subsurface Disposal Area

[Location of sampling sites shown in figs. 2-2 and 2-3; redox state distributions in percent; \* water assumed to be at equilibrium with atmospheric O<sub>2</sub>]

Sampling site	log $P_{CO_2}$	log $P_{O_2}$	% Np (V)	% Np (VI)	% Pu(IV)	% Pu (V)	% Pu(VI)
Big Lost River below INEEL diversion	-1.08	-0.7*	93.8	6.23	10.5	88.6	0.878
USGS 92 (perched water)	-3.03	-0.7*	33.0	67.0	0.137	99.8	0.114
EBR 1	-3.1	-0.74	88.2	11.8	0.0437	99.9	0.0509
NPR Test	-2.76	-0.63	66.9	33.1	0.167	99.8	0.0934
P&W 2	-2.86	-0.63	61.2	38.8	0.117	99.8	0.0902
USGS 8	-2.92	-0.7	59.8	40.3	0.115	99.8	0.0840
USGS 19	-2.53	-0.74	82.6	17.4	0.278	99.7	0.0896
USGS 112	-2.74	-0.78	85.2	14.9	0.133	99.8	0.0764
RWMC Production	-2.93	-0.69	65.0	35.0	0.103	99.8	0.0800
USGS 87	-3.05	-0.59	77.6	22.5	0.0530	99.9	0.0671
USGS 89	-3.38	-0.53	80.4	19.7	0.0174	100.	0.0526
USGS 90	-3.02	-0.62	73.8	26.3	0.0638	99.9	0.0707

Table 4-6. Measured pH values and calculated aqueous speciation of Np and Pu in water samples from sites at or near the Subsurface Disposal Area. The three dominant aqueous species of Np and Pu are reported along with their molar concentrations and redox state

Locations of sampling sites shown in figs. 2-2 and 2-3; Abbreviations: aq., aqueous; conc., concentration; st., state]

Sampling site	pH	1 <sup>st</sup> Np aq. conc. redox st.	2 <sup>nd</sup> Np aq. conc. redox st.	3 <sup>d</sup> Np aq. conc. redox st.	1 <sup>st</sup> Pu aq. conc. redox st.	2 <sup>nd</sup> Pu aq. conc. redox st.	3 <sup>d</sup> Pu aq. conc. redox st.
Big Lost River below INEEL diversion	6.4	NpO <sub>2</sub> <sup>+</sup> 9.15E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 5.04E-10 (VI)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 2.29E-10 (V)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 8.86E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 1.05E-9 (IV)	PuO <sub>2</sub> CO <sub>3</sub> 7.62E-11 (VI)
USGS 92 (perched water)	8.39	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>-4</sup> 3.65E-9 (VI)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 3.05E-9 (VI)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 2.41E-9 (V)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.98E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 1.29E-11 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 7.62E-11 (VI)
EBR 1	8.2	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 4.58E-9 (V)	NpO <sub>2</sub> <sup>+</sup> 4.22E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 8.94E-10 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.99E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 4.30E-12 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 4.08E-12 (VI)
NPR Test	8.0	NpO <sub>2</sub> <sup>+</sup> 3.52E-9 (V)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 3.16E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 2.51E-9 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.98E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 1.64E-11 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 7.26E-12 (VI)
P&W 2	8.0	NpO <sub>2</sub> <sup>+</sup> 3.69E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 3.19E-9 (VI)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 2.43E-9 (V)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.98E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 1.16E-11 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 6.10E-12 (VI)
USGS 8	8.1	NpO <sub>2</sub> <sup>+</sup> 3.06E-9 (V)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 2.90E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 3.06E-9 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.98E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 1.13E-11 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 6.34E-12 (VI)
USGS 19	7.8	NpO <sub>2</sub> <sup>+</sup> 5.06E-9 (V)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 3.19E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 1.42E-9 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.97E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 2.76E-11 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 6.71E-12 (VI)
USGS 112	7.8	NpO <sub>2</sub> <sup>+</sup> 6.20E-9 (V)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 2.30E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 1.27E-9 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.98E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 1.32E-11 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 4.66E-12 (VI)
RWMC Production	8.1	NpO <sub>2</sub> <sup>+</sup> 3.360E-9 (V)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 3.13E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 2.67E-9 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.98E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 1.01E-11 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 6.07E-12 (VI)
USGS 87	8.1	NpO <sub>2</sub> <sup>+</sup> 4.50E-9 (V)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 3.24E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 1.82E-9 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.99E-9 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 5.24E-12 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 4.72E-12 (VI)
USGS 89	8.3	NpO <sub>2</sub> <sup>+</sup> 4.37E-9 (V)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 3.65E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 1.54E-9 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 1.00E-8 (V)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 3.56E-12 (VI)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 1.71E-12 (IV)
USGS 90	8.1	NpO <sub>2</sub> <sup>+</sup> 4.17E-9 (V)	NpO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 3.20E-9 (V)	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 2.09E-9 (VI)	PuO <sub>2</sub> CO <sub>3</sub> <sup>-</sup> 9.99E-8 (V)	Pu(CO <sub>3</sub> ) <sub>3</sub> <sup>-2</sup> 6.30E-12 (IV)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-2</sup> 5.07E-12 (VI)

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Table 4-7. Calculated distribution of Np and Pu surface complexes on goethite and molar ratios of total sorbed to total aqueous concentrations for Np ( $K_r$  Np) and Pu ( $K_r$  Pu) for water samples from sites at or near the Subsurface Disposal Area. The three dominant surface complexes of Np and Pu are reported along with their molar concentrations and redox state. Goethite adsorption site concentration was  $5 \times 10^{-6}$  mole per kg of water.

[Locations of sampling sites shown in figs. 2-2 and 2-3. Abbreviations: s.c., surface complexes; conc., concentration; st., state]

Sampling site	$K_r$ Np	$K_r$ Pu	1 <sup>st</sup> Np s.c. conc. redox st.	2 <sup>nd</sup> Np s.c. conc. redox st.	3 <sup>d</sup> Np s.c. conc. redox st.	1 <sup>st</sup> Pu s.c. conc. redox st.	2 <sup>nd</sup> Pu s.c. conc. redox st.	3 <sup>d</sup> Pu s.c. conc. redox st.
Big Lost River near the INEEL diversion	3.69	8.1E-4	$(>O)_2NpO_2^-$ 3.58E-8 (V)	$>OHNpO_2^+$ 5.44E-10 (V)	$>OH_2NpO_2OH^+$ 5.44E-10 (V)	$>OPuO_2OH^-$ 5.63E-12 (V)	$>OPuO_2$ 1.24E-12 (V)	$>OHPuO_2OH$ 1.24E-12 (V)
USGS 92 (perched water)	198	5.5E-3	$(>O)_2NpO_2^-$ 1.98E-6 (V)	$>ONpO_2OH^-$ 8.82E-10 (V)	$>ONpO_2$ 4.57E-10 (V)	$>OPuO_2OH^-$ 5.39E-11 (V)	$>OPuO_2$ 7.35E-13 (V)	$>OHPuO_2OH$ 7.34E-13 (V)
EBR 1	204	3.9E-3	$(>O)_2NpO_2^-$ 2.04E-6 (V)	$>ONpO_2$ 1.20E-9 (V)	$>OHNpO_2OH$ 1.20E-9 (V)	$>OPuO_2OH^-$ 3.68E-11 (V)	$>OPuO_2$ 1.02E-12 (V)	$>OHPuO_2OH$ 1.02E-12 (V)
NPR Test	182	3.6E-3	$(>O)_2NpO_2^-$ 1.82E-6 (V)	$>ONpO_2$ 8.83E-10 (V)	$>OHNpO_2OH$ 8.83E-10 (V)	$>OPuO_2OH^-$ 3.34E-11 (V)	$>OPuO_2$ 1.09E-12 (V)	$>OHPuO_2OH$ 1.09E-12 (V)
P&W 2	181	4.6E-3	$(>O)_2NpO_2^-$ 1.81E-6 (V)	$>OHNpO_2^+$ 9.77E-10 (V)	$>OH_2NpO_2OH^+$ 9.77E-10 (V)	$>OPuO_2OH^-$ 4.32E-11 (V)	$>OPuO_2$ 1.50E-12 (V)	$>OHPuO_2OH$ 1.50E-12 (V)
USGS 8	190	4.4E-3	$(>O)_2NpO_2^-$ 1.90E-6 (V)	$>ONpO_2$ 8.90E-10 (V)	$>OHNpO_2OH$ 8.90E-10 (V)	$>OPuO_2OH^-$ 4.14E-11 (V)	$>OPuO_2$ 1.19E-12 (V)	$>OHPuO_2OH$ 1.19E-12 (V)
USGS 19	164	2.8E-3	$(>O)_2NpO_2^-$ 1.64E-6 (V)	$>OHNpO_2^+$ 1.26E-9 (V)	$>OH_2NpO_2OH^+$ 1.26E-9 (V)	$>OPuO_2OH^-$ 2.55E-11 (V)	$>OPuO_2$ 1.14E-12 (V)	$>OHPuO_2OH$ 1.14E-12 (V)
USGS 112	171	4.4E-3	$(>O)_2NpO_2^-$ 1.71E-6 (V)	$>OHNpO_2^+$ 1.36E-9 (V)	$>OH_2NpO_2OH^+$ 1.36E-9 (V)	$>OPuO_2OH^-$ 4.03E-11 (V)	$>OPuO_2$ 1.75E-12 (V)	$>OHPuO_2OH$ 1.75E-12 (V)
RWMC Prod.	192	4.3E-3	$(>O)_2NpO_2^-$ 1.92E-6 (V)	$>ONpO_2$ 9.40E-10 (V)	$>OHNpO_2OH$ 9.40E-10 (V)	$>OPuO_2OH^-$ 4.03E-11 (V)	$>OPuO_2$ 1.16E-12 (V)	$>OHPuO_2OH$ 1.16E-12 (V)
USGS 87	197	4.7E-3	$(>O)_2NpO_2^-$ 1.97E-6 (V)	$>ONpO_2$ 1.14E-9 (V)	$>OHNpO_2OH$ 1.14E-9 (V)	$>OPuO_2OH^-$ 4.43E-11 (V)	$>OPuO_2$ 1.36E-12 (V)	$>OHPuO_2OH$ 1.36E-12 (V)
USGS 89	215	6.3E-3	$(>O)_2NpO_2^-$ 2.14E-6 (V)	$>ONpO_2OH^-$ 1.49E-9 (V)	$>ONpO_2$ 1.25E-9 (V)	$>OPuO_2OH^-$ 6.03E-11 (V)	$>OPuO_2$ 1.33E-12 (V)	$>OHPuO_2OH$ 1.33E-12 (V)
USGS 90	196	4.6E-3	$(>O)_2NpO_2^-$ 1.96E-6 (V)	$>ONpO_2$ 1.08E-9 (V)	$>OHNpO_2OH$ 1.08E-9 (V)	$>OPuO_2OH^-$ 4.36E-11 (V)	$>OPuO_2$ 1.31E-12 (V)	$>OHPuO_2OH$ 1.31E-12 (V)

Although the thermodynamic data base used for these calculations included Np and Pu complexes with  $\text{SO}_4$ ,  $\text{NO}_3$ , F, and  $\text{PO}_4$ , concentrations of these components in the water samples were not large enough for any of the resulting Pu and Np complexes to be important. Water in direct contact with the radionuclide waste, however, probably has a significantly different chemistry from that of the water samples given in table 4-4 and may have large concentrations of  $\text{NO}_3$ ,  $\text{PO}_4$ , and other complexants. Although these complexants may increase the aqueous stability of Np and Pu, the pH and redox character of the waters also would be important variables in determining the aqueous stability, or the mobility, of Np and Pu.

The surface complexation speciation calculations reflect the aqueous speciation calculations in that the strong complexation of aqueous Pu with carbonate impedes surface complexation of Pu to the goethite surface, at least according to the thermodynamic model. Very little Pu was sorbed on the goethite surface; the aqueous solution generally contained at least 200 times more Pu ( $K_r \text{ Pu} = 4.5\text{E-}3$  on average for the ground-water samples). The PHREEQC speciation calculations were repeated using identical input data, except that the Np data was omitted to determine if Np competition for surface sites affected the sorption of Pu in the previous calculations. Although the results are not shown here, the conclusion was that although Np competition did have some effect on the sorption of Pu in some water samples, Pu sorption was still very small. The largest  $K_r \text{ Pu}$  value was 0.11 (for water from well USGS 89), and the values for most other water samples were one to two orders of magnitude lower.

The large concentrations of the aqueous neptunyl species relative to those of the neptunyl carbonate species, indicate a small amount of aqueous complexation by carbonate and, therefore, that Np was strongly sorbed to the goethite surface in the INEEL ground-water samples, which all had pH values of about 8. The speciation of the various water samples and of the equilibrium goethite surface generally resulted in an amount of sorbed Np that was about 200 times larger than the amount of aqueous Np; however, because of a lower pH value of 6.4 in the BLR water sample, the amount of sorbed Np in this sample was significantly smaller (a  $K_r$  value near 4).

The  $K_r$  values calculated for Np and Pu were generally proportional to the amount of goethite surface assumed present for each kg of water. If the concentration of goethite surface sites is increased by a factor of 10, the amount of Np and Pu sorption generally also will increase by a factor of 10. PHREEQC simulations confirmed this theory, except for the simulation of water from the BLR,

for which the  $K_r \text{ Pu}$  value increased by a factor of 15 as a result of the tenfold increase in goethite surface (the  $K_r \text{ Np}$  value increased by a factor of 10).

Because of a lack of appropriate data for the site concentrations of sediments from the INEEL, the concentration of surface sites chosen for our speciation example was derived from a calculation example given by Dzombak and Morel (1990). Field and laboratory studies of a sand and gravel aquifer at the USGS research site in Falmouth, Mass., on Cape Cod indicate that, if sediments are uniformly coated with a thin layer of iron oxyhydroxide, the site concentration is about  $10^{-2} \text{ M}$  (Davis and others, 1998). Calculations by Gary Curtis (oral commun., 1999) for the USGS research site, a sandy silt aquifer, in Bemidji, Minn. indicate a similar surface site concentration of about  $10^{-2} \text{ M}$ . If properties of the interbed sediments at the INEEL are similar to those at the Bemidji and Cape Cod sites, then the  $K_r$  values calculated in this report for both Pu and Np at the INEEL are about 2,000 times too small. If speciation calculations for the BLR sample are disregarded, and this larger surface site concentration of  $10^{-2} \text{ M}$  is combined with our speciation calculations, then a  $K_r$  value of about  $4 \times 10^4$  would be applicable for Np sorption and a  $K_r$  value of 9 would be applicable for Pu sorption in the interbed sediments. These  $K_r$  values can be used to estimate the retardation of Pu or Np relative to the advective movement of water by calculation of a retardation factor (defined in equation 4.4 in section 4.3). The calculated retardation factors are 10 for Pu and  $4 \times 10^4$  for Np. It is more difficult to estimate the sorption capacity and, consequently, the retardation factors applicable to the transport of Np and Pu in the INEEL basalts, but they probably would be significantly smaller than those of the interbed sediments.

Because of the lack of field or laboratory data on the amount and type of sorption sites on INEEL sediments and basalt surfaces, the speciation calculations presented here cannot be used to predict the retardation of Np and Pu. Nevertheless, the calculations indicate the very strong aqueous complexation of Pu with carbonate and the significantly stronger sorption of Np relative to that of Pu. Transport of Pu at the INEEL could be limited by the reducing conditions in the soil or ground-water environment. In reducing conditions, Pu(IV) probably would be the dominant state of Pu, instead of Pu(V) and Pu(VI), which are the stable oxidation states in oxygenated conditions. When and where present, reducing conditions probably significantly limit the mobility of Pu. Reducing conditions probably occur most commonly in the source areas of radioactive waste emplacement (because of the associated organic matter and metallic substances present) and

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also possibly in relatively impermeable (clayey), organic-carbon-containing zones in the interbed sediments. Although relatively uncommon, some organic-rich zones in the interbed sediments have been found (Rightmire and Lewis, 1987a). Fe(II)-containing minerals in the basalts and in the interbeds also potentially could reduce Pu(V) and Pu(VI); in hydraulically conductive zones, however, the surface of these minerals already should have been oxidized extensively by the oxygenated ground waters. The large concentrations of DO and inorganic carbon in all ground-water samples from the INEEL used in this study indicate the possibility of Pu(V), and Pu(VI) transport in the SRP aquifer. In addition to reduction processes, other sorption and transformation processes not considered in this modeling study potentially could limit the mobility of Pu, for example: (1) the sorption of Pu(V) and Pu(VI) by calcite, and (2) the disproportionation of Pu(V) into Pu(IV) and Pu(VI) through the sorption by goethite (Keeny-Kennicutt and Morse, 1985).

##### 4.3.2.4 Additional speciation calculations for Np and Pu

This section presents additional speciation calculations for the water samples discussed in the previous section (4.3.2.3); however, thermodynamic data for Np and Pu used in the calculations were obtained from a different data base. The same conditions that were assumed for the previous Np and Pu speciation calculations also were

assumed for these calculations. Also, for the reasons discussed in the previous section, the calculations presented here should be considered only generally illustrative of Np and Pu behavior in aqueous environments.

Thermodynamic data for aqueous Pu and Np also was obtained in the PHREEQC format from the EQ3/6 data base by David Turner (Southwest Research Institute, written commun., 1999). The EQ3/6 data base, like the ANSTO and HATCHES data bases, generally did not include any enthalpy data; consequently, the temperature dependence of Np and Pu speciation at temperatures other than 25°C could not be properly modeled. As in our previous calculations, Turner's (1995) surface complexation constants were used to simulate Pu(IV), Pu(V), and Np(V) sorption by goethite.

Table 4-8 shows the redox-state distributions calculated by using data from the ANSTO and EQ3/6 data bases. Calculations of Pu redox-state distributions based on the two data bases are significantly different: those based on the ANSTO (and HATCHES) data bases predict that the Pu was present predominantly as Pu(V), and those based on the EQ3/6 data base indicate that Pu was present predominantly as Pu(VI).

Table 4-8. Calculated aqueous Np and Pu redox-state distributions at equilibrium for selected water samples from the Idaho National Engineering and Environmental Laboratory determined using either the ANSTO or the EQ3/6 data bases

Sampling site; Data source	% Np (V)	% Np (VI)	% Pu (IV)	% Pu (V)	% Pu (VI)
Big Lost River; ANSTO	93.8	6.23	10.5	88.6	0.878
Big Lost River; EQ3/6	100	0.003	0.000	0.003	100
USGS 92 (perched water); ANSTO	33.0	67.0	0.137	99.8	0.114
USGS 92 (perched water); EQ3/6	84.2	15.8	0.001	0.003	100
NPR Test; ANSTO	66.9	33.1	0.167	99.8	0.093
NPR; EQ3/6	98.5	1.49	0.000	0.004	100
USGS 112; ANSTO	85.2	14.9	0.133	99.8	0.076
USGS 112; EQ3/6	99.8	0.228	0.000	0.007	100
RWMC Production; ANSTO	65.0	35.0	0.103	99.8	0.080
RWMC Production; EQ3/6	98.6	1.30	0.000	0.005	100
USGS 89; ANSTO	80.4	19.7	0.017	100	0.053
USGS 89; EQ3/6	99.4	0.565	0.001	0.008	100

The calculations of Np redox-state distributions based on the two data bases are also significantly different. Whereas the calculations based on the EQ3/6 data base indicate that almost all the Np was present in the Np(V), those based on the ANSTO (and HATCHES) data base indicate that large amounts of Np(VI) also were present. The reasons for these differences can be determined from table 4-9, which shows the concentrations and redox states of the dominant Pu and Np species calculated on the basis of both the ANSTO and EQ3/6 data bases. The association constant in the EQ3/6 data base for the Pu(VI) species  $\text{PuO}_2\text{CO}_3$ , the dominant aqueous Pu species in the EQ3/6 results, is 3 orders of magnitude larger than the association constant for this species in the ANSTO data base. Additionally, the Pu(V) species  $\text{PuO}_2\text{CO}_3^-$ , the dominant species in the ANSTO results, is not present in the EQ3/6 results. In contrast, the association constant in the EQ3/6 data base for the Np(VI) species  $\text{NpO}_2(\text{CO}_3)_2^{2-}$ , a dominant species in the ANSTO results, is 3 orders of magnitude smaller than the association constant for this species in the ANSTO data base. The EQ3/6 results also show the dominance of the Np(V) species  $\text{NpO}_2\text{OH}$ . The association constant in the EQ3/6 data base for this species is 2 orders of magnitude larger than the association constant in the ANSTO data base.

Because of the differences in the speciations of Np and Pu predicted by the ANSTO and EQ3/6 data bases, the  $K_r$  values calculated from the SCM data (and based on the same conditions described in section 4.3.2.3 of total surface site concentration of  $5 \times 10^{-6}$  mol/L) were compared. The results are presented in table 4-10.

The EQ3/6 results indicate generally 5 to 10 percent larger  $K_r$  values for Np than the ANSTO results, and consequently, greater retardation during transport. Interestingly, the  $K_r$  Pu values calculated from the EQ3/6 data were also generally larger than those calculated from the ANSTO data (except for the BLR water sample), by as much as a factor of 3.6 (for the sample from well EBR 1). If the surface site concentration increases from  $5 \times 10^{-6}$  mol/L to  $10^{-2}$  mol/L and  $K_r$  values increase linearly by a factor of 2,000, the  $K_r$  Pu value for the sample from well USGS 89 would increase from 12.6, the value calculated from the ANSTO data, to 32.

The additional speciation calculations presented in this section illustrate the many uncertainties that remain concerning thermodynamic data for Pu and Np aqueous speciation. The uncertainties involved in thermodynamic modeling of Pu and Np sorption and in any predictions of Np and Pu transport by such thermodynamic models can be expected to be even greater, because the results depend not only on the aqueous thermodynamic data, but also

sorption data and the properties of the interbed sediments and basalts. Nevertheless, thermodynamic speciation results can illustrate the potential dependencies of sorption processes on aqueous and surface chemical compositions and on mineralogical parameters, and can be used to estimate the effects of compositional and mineralogical changes.

Table 4-10.  $K_r$  values of Np and Pu surface complexes on goethite for water samples from the Idaho National Engineering and Environmental Laboratory, calculated on the basis of data from the ANSTO and EQ3/6 data bases.

Sampling site	$K_r$ Np; ANSTO	$K_r$ Np; EQ3/6	$K_r$ Pu; ANSTO	$K_r$ Pu; EQ3/6
Big Lost River below INEEL diversion	3.69	3.69	8.1E-4	1.2E-05
USGS 92 (perched water)	198	225	5.5E-3	1.1E-02
EBR 1	204	211	3.9E-3	1.4E-02
NPR Test	182	199	3.6E-3	4.5E-03
P&W 2	181	199	4.6E-3	4.2E-03
USGS 8	190	208	4.4E-3	5.5E-03
USGS 19	164	176	2.8E-3	3.5E-03
USGS 112	171	180	4.4E-3	4.6E-03
RWMC Production	192	208	4.3E-3	6.0E-03
USGS 87	197	208	4.7E-3	7.7E-03
USGS 89	215	222	6.3E-3	1.6E-02
USGS 90	196	208	4.6E-3	7.2E-03

### 4.3.3 Summary

This section has demonstrated that speciation can be important in controlling the transport of actinides below the SDA. Critical factors involving speciation that affect actinide transport are the determination of the redox state of the actinide, determination of the aqueous species, and determination of the surface species. Redox state is especially important for determining transport of Pu and U. Pu(IV) and U(IV) are both very insoluble and, therefore, relatively immobile. However, it is difficult to assess the factors that control the oxidation state of these species in the heterogeneous environment below the SDA that consists of both fractured basalts and sedimentary interbeds. It is comparatively easier and, therefore, the primary focus of this section, to compute the effects of different aqueous compositions and different SCM's on the  $K_r$  values. The calculations were made in spite of the many

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Table 4-9. Concentrations and redox states of the three dominant species of Np and Pu in water samples from the Idaho National Engineering and Environmental Laboratory calculated on the basis of the ANSTO and EQ3/6 data bases

[Abbreviations: aq., aqueous; conc., concentration; st., state]

Sampling site; data base	1 <sup>st</sup> Np aq. conc. redox st.	2 <sup>nd</sup> Np aq. conc. redox st.	3 <sup>d</sup> Np aq. conc. redox st.	1 <sup>st</sup> Pu aq. conc. redox st.	2 <sup>nd</sup> Pu aq. conc. redox st.	3 <sup>d</sup> Pu aq. conc. redox st.
Big Lost River below INEEL diversion; ANSTO	$\text{NpO}_2^+$ 9.15E-9 (V)	$\text{NpO}_2(\text{CO}_3)_2^{-2}$ 5.04E-10 (VI)	$\text{NpO}_2\text{CO}_3^-$ 2.29E-10 (V)	$\text{PuO}_2\text{CO}_3^-$ 8.86E-9 (V)	$\text{Pu}(\text{CO}_3)_3^{-2}$ 1.05E-9 (IV)	$\text{PuO}_2\text{CO}_3$ 7.62E-11 (VI)
Big Lost River below INEEL diversion; EQ3/6	$\text{NpO}_2^+$ 9.95E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 3.89E-11 (V)	$\text{NpO}_2\text{OH}$ 1.13E-11 (V)	$\text{PuO}_2\text{CO}_3$ 1.00E-8 (VI)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 4.50E-13 (VI)	$\text{PuO}_2\text{F}_3^-$ 2.94E-13 (VI)
USGS 92 (perched water); ANSTO	$\text{NpO}_2(\text{CO}_3)_3^{-4}$ 3.65E-9 (VI)	$\text{NpO}_2(\text{CO}_3)_2^{-2}$ 3.05E-9 (VI)	$\text{NpO}_2\text{CO}_3^-$ 2.41E-9 (V)	$\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V)	$\text{Pu}(\text{CO}_3)_3^{-2}$ 1.29E-11 (IV)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 7.62E-11 (VI)
USGS 92 (perched water); EQ3/6	$\text{NpO}_2^+$ 4.84E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 2.82E-9 (V)	$\text{NpO}_2(\text{CO}_3)_3^{-4}$ 1.58E-9 (VI)	$\text{PuO}_2\text{CO}_3$ 9.86E-9 (VI)	$\text{PuO}_2(\text{CO}_3)_3^{-4}$ 7.46E-11 (VI)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 5.96E-11 (VI)
NPR Test; ANSTO	$\text{NpO}_2^+$ 3.52E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 3.16E-9 (V)	$\text{NpO}_2(\text{CO}_3)_2^{-2}$ 2.51E-9 (VI)	$\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V)	$\text{Pu}(\text{CO}_3)_3^{-2}$ 1.64E-11 (IV)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 7.26E-12 (VI)
NPR Test; EQ3/6	$\text{NpO}_2^+$ 7.79E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 1.57E-9 (V)	$\text{NpO}_2\text{OH}$ 4.74E-10 (V)	$\text{PuO}_2\text{CO}_3$ 9.98E-9 (VI)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 1.85E-11 (VI)	$\text{PuO}_2(\text{CO}_3)_3^{-4}$ 5.53E-12 (VI)
USGS 112; ANSTO	$\text{NpO}_2^+$ 6.20E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 2.30E-9 (V)	$\text{NpO}_2(\text{CO}_3)_2^{-2}$ 1.27E-9 (VI)	$\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V)	$\text{Pu}(\text{CO}_3)_3^{-2}$ 1.32E-11 (IV)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 4.66E-12 (VI)
USGS 112; EQ3/6	$\text{NpO}_2^+$ 8.92E-9 (VI)	$\text{NpO}_2\text{CO}_3^-$ 7.15E-10 (V)	$\text{NpO}_2\text{OH}$ 3.27E-10 (V)	$\text{PuO}_2\text{CO}_3$ 9.99E-9 (VI)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 7.99E-12 (VI)	$\text{PuO}_2(\text{OH})_2$ 2.14E-12 (VI)
RWMC Production; ANSTO	$\text{NpO}_2^+$ 3.360E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 3.13E-9 (V)	$\text{NpO}_2(\text{CO}_3)_2^{-2}$ 2.67E-9 (VI)	$\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V)	$\text{Pu}(\text{CO}_3)_3^{-2}$ 1.01E-11 (IV)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 6.07E-12 (VI)
RWMC Production; EQ3/6	$\text{NpO}_2^+$ 7.84E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 1.46E-9 (V)	$\text{NpO}_2\text{OH}$ 5.49E-10 (V)	$\text{PuO}_2\text{CO}_3$ 9.98E-9 (VI)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 1.79E-11 (VI)	$\text{PuO}_2(\text{CO}_3)_3^{-4}$ 5.93E-12 (VI)
USGS 89; ANSTO	$\text{NpO}_2^+$ 4.37E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 3.65E-9 (V)	$\text{NpO}_2(\text{CO}_3)_2^{-2}$ 1.54E-9 (VI)	$\text{PuO}_2\text{CO}_3^-$ 1.00E-8 (V)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 3.56E-12 (VI)	$\text{Pu}(\text{CO}_3)_3^{-2}$ 1.71E-12 (IV)
USGS 89; EQ3/6	$\text{NpO}_2^+$ 7.64E-9 (V)	$\text{NpO}_2\text{CO}_3^-$ 1.38E-9 (V)	$\text{NpO}_2\text{OH}$ 9.08E-10 (V)	$\text{PuO}_2\text{CO}_3$ 9.97E-9 (VI)	$\text{PuO}_2(\text{CO}_3)_2^{-2}$ 1.63E-11 (VI)	$\text{PuO}_2(\text{OH})_2$ 9.47E-12 (VI)



uncertainties and problems with the available thermodynamic data. These limitations include a lack of consistent thermodynamic data for all important reactions, the inability to describe and quantify Pu hydroxide polymerization reactions, little knowledge of actinide complexation with natural organic matter, and lack of a site-specific surface complexation model. Despite these limitations,  $K_d$  values were calculated for 1 surface-water sample, 1 perched-water sample, and 10 ground-water samples. Even if the surface-water sample is ignored, the calculated  $K_d$  values for Am varied by 400 percent, for U by 3,000 percent, for Np by 25 percent, and for Pu by 55 percent. These variations were due only to differences in aqueous compositions among the different water samples. For Am and U, the range of  $K_d$ s also reflects variations introduced by considering several SCMs. One significant limitation of this approach is that only one water-sample analysis was available for the perched-water sample (USGS 92). This is important because (1)  $K_d$ s of Pu in water from well USGS 92 were relatively large and  $K_d$ s of U were relatively small, and (2) the transport away from the SDA may be controlled by sorption from perched water in the sedimentary interbeds.

#### 4.4 Applicability of the local equilibrium concept to actinide transport

Distribution coefficients theoretically apply only to reversible first-order reactions at local equilibrium. Actinide sorption and desorption reactions with minerals often are affected by several kinetic processes. These include:

- (1) The rate of chemical or physical sorption reactions between an actinide and a mineral surface. Generally, these reactions are relatively fast, although there is often a slow component that could require weeks to attain equilibrium.

- (2) Diffusion of actinides to or from reaction sites in zones of immobile water. This diffusion increases the time required to attain equilibrium. The immobile water can be a layer on the grain surface, within crevices or pits in the grain, in dead-end pores between tightly packed grains, in fractures, or in the interlayer of expandable clay minerals. If the diffusion rate of an actinide is slow compared with the transport rate in the flowing phase, physical nonequilibrium occurs.

- (3) Mineralogical changes in the sorbing phase. For example, freshly precipitated ferrihydrite has a relatively large sorption capacity because its unordered structure results in a large surface area with excess charge. As ferrihydrite recrystallizes to more ordered structures such as

goethite, surface area and sorption capacity decrease. Other slow diagenetic reactions involving clay minerals also will slowly change the sorption property of a solid.

##### 4.4.1 Chemically-mediated kinetics

Several laboratory batch experiments have shown that sorption of actinides is characterized by a rapid initial decrease in aqueous concentration followed by a more gradual approach to equilibrium that can take weeks. Many studies have attributed this decrease in aqueous concentration as sorption without demonstrating that other processes, such as redox or precipitation, could be ignored. The rate of approach to equilibrium in laboratory experiments often is affected by experimental conditions, the nature of the solid and aqueous phases, and the type and redox state of the actinide. For example, batch experiments are conducted by using a variety of agitation techniques. Violent agitation in reciprocating shakers can slowly abrade grains and cause gradual changes in the sorbing surface that can be interpreted as chemical reaction kinetics. Other agitation methods may incompletely mix sediment and solution. Diffusion of actinides to sorption sites in unmixed sediment at the bottom of a beaker can be interpreted as slow chemical reaction kinetics.

Use of a solid phase that is not in chemical equilibrium with the aqueous phase can induce apparent actinide sorption kinetics. For example, when a rock is crushed for use in sorption experiments, weathering reactions on the fresh surface of the grains can slowly change the mineralogy of the solid and the sorption properties of the actinide (Barney, 1981).

Barney (1978) evaluated sorption of Am, Np, and Pu in batch experiments as a function of time. Crushed basalt, crushed granite, and crushed argillite were used. An initial rapid sorption reaction, complete within 5 minutes, was followed by a slow reaction that apparently resulted from changes in the composition of the rock surface. Equilibrium concentrations were not attained within 145 days. Bulk solution chemistry continued to change as a result of weathering of the freshly crushed mineral faces; therefore, it was difficult to conclude whether the slow sorption was a result of a slow reaction with a stable mineral phase or the changing mineralogy. The release of a relatively large amount of silica appeared to increase the solubility of Am and Pu. This result also complicated interpretation of the data.

Newman and others (1995) determined sorption rate constants for sorption of U by crushed basalt and a composite interbed sediment from the INEEL. The time required to reach equilibrium with crushed basalt was 61

hours. The time required to reach equilibrium with the interbed sediment was 103 hours. However, more than 90 percent of the sorption by both solids took place within the first 4 hours of the experiment.

In another set of batch experiments by Friedman and Kelmers (1990), sorption of U by a soil increased throughout the 168-hour length of the experiments; however, 96 percent of the U was sorbed within the first 24 hours.

Rhodes (1957) used batch experiments to measure Pu sorption by a soil from Hanford, Wash. To attain 99.9-percent adsorption, 360 hours were required; 86 percent of the Pu was sorbed within 0.08 hours. Nelson and others (1985) noted that reaction kinetics for Pu sorption and the amount sorbed were affected by complexation with DOC. More Pu remained in the aqueous phase as the concentration of DOC increased. The time required to achieve equilibrium also increased as DOC increased.

Sheppard and others (1979) measured and noted three distinct phases in the sorption of Am and Np by four soils from the INEEL as a function of time. The first phase was a rapid quasi-exponential decrease in aqueous concentration; the second phase was a slower exponential decrease in aqueous concentration; the final phase was the stabilization of the concentration as equilibrium was attained. Their data are quantified by the number of days required for Am and Np concentrations to decrease to 37 percent of the initial concentration. For the sorption of Np, 13, 14, 39, and 52 days were required. For the sorption of Am, 51, 202, and 361 days were required. Equilibrium was attained more rapidly as the grain size of the soils increased and the cation exchange capacity decreased. The soil that equilibrated least rapidly with Am and Np had the largest clay and silt content and cation exchange capacity. This slower equilibration time could indicate exchange with ions in interlayer positions of the clay minerals and could be partially controlled by diffusion.

Rock type also has been shown to affect equilibration time for Am and Pu (Seitz and others, 1978). Equilibrium concentrations were attained relatively quickly (less than 5 hours) in carbonates such as limestone, dolomite and marble. More than 100 hours were required for equilibrium in basalts and metamorphic rocks. Equilibration times were between 5 and 100 hours in sandstone and granite. The rate of decrease in aqueous concentration generally was faster for Pu than for Am.

#### 4.4.2 Transport-controlled kinetics

Nonequilibrium transport of solutes through porous media occurs when ground-water velocities are sufficiently fast to prevent attainment of chemical and physical

equilibrium. Transport through the interbeds at the INEEL is likely to be slow enough for reactions to approach, if not to attain, equilibrium. Transport through basalt fractures and vesicles could be too fast to allow sufficient time for equilibration.

Kumata and Vandergraaf (1998) eluted solutions spiked with Np(IV) through columns packed with highly weathered, crushed granite. At a low flow velocity of 0.03 m/d, Np was detected only in the first few centimeters of the column. As velocities increased, Np was detected farther down the column. At 0.3 m/d, Np began to elute from the column. Np(IV) is very insoluble, and transport may be indicative of a sorbed phase or of a  $\text{NpO}_2$  colloid. Regardless of the mechanism, the experimental data show the effect of flow rate on the transport of Np.

The asymmetrical shape of breakthrough curves for Np(V) in column experiments has been modeled by using the advective-dispersive model and a first-order kinetic term to account for mass transfer of Np between the flowing phase and stagnant water in side pores (Andre and others, 1998).

Data from the Large Scale Infiltration Test (LSIT) conducted at the INEEL indicate the presence of a complex network of flowpaths in the basalt (Wood and Norrell, 1996). Transport of nonreactive tracers indicates that moisture infiltrates mostly along preferential-flow paths under unsaturated flow conditions. Transport velocities varied greatly.

Information is insufficient to reliably assess whether actinides and sediments at the INEEL are in chemical equilibrium. The chemical and physical nature of the waste at the SDA is unknown. The speciation of actinides could have an effect on equilibrium. For example, a Pu organic complex could sorb at a different rate than a Pu fluoride complex. However, previous studies at the INEEL indicate that sorption of actinides by interbed sediments is relatively rapid, and most sorption occurs within 24 hours. There is also evidence for a slower sorption process in which equilibrium could take weeks to attain; however, for the purpose of risk assessment analysis, the assumption of chemical equilibrium appears to be reasonable. Flow velocities through the interbed layers appear to be slow enough to allow time for sorption reactions to attain equilibrium.

There could be insufficient time for equilibrium to occur in basalt fractures because of faster flow velocities. Also, there is evidence from the LSIT for diffusion into zones of stagnant water, which would increase the time needed to attain equilibrium. However, because of the relatively small amount of rainfall and infiltration at the INEEL, sustained rapid flow through fractures may be

limited. The slower velocities associated with short intermittent periods of recharge could allow enough time for reactions to approach equilibrium.

## 4.5. Colloid-facilitated transport of actinides

Transport of actinides beneath the SDA may be enhanced by association with colloids and larger particles capable of being transported by water. This evaluation of colloid-facilitated transport is organized into three sections. The first section is a general discussion of colloid formation and mobility; the next section is a review of previous studies of actinides associated with colloids; and the final section is a discussion of evidence for colloid-facilitated transport of actinides at the INEEL.

### 4.5.1 Colloid definition and mobility

The definition of a colloid varies; it generally is based on size and is often an operational definition based on the techniques used to separate the solid phase from the aqueous phase. Vilks and others (1998) defined a colloid as a particle small enough to be kept in suspension by Brownian motion. Suspended particles larger than colloids require water turbulence to stay in suspension and are less likely to be transported. Particles with diameters of less than 10  $\mu\text{m}$  generally are considered to be colloids (fig. 4-8 from Stumm and Morgan, 1981).

Colloids can be rock and mineral fragments, mineral precipitates and weathering products, macromolecular components of DOC such as humic substances, biocolloids such as micro-organisms, and microemulsions of nonaqueous-phase liquids (McCarthy and Zachara, 1989). Colloids can form from condensation or homogeneous nucleation of particles from dissolved species when a mineral phase is supersaturated. Colloids can form as alteration products of *in situ* minerals, or they can be transported from somewhere else.

Particles can be released into solution by various processes such as the (1) disruption of fragile aggregates by changes in ionic strength (low ionic strength tends to increase colloid stability) or by hydrodynamic force, (2) mechanical grinding of mineral surfaces, (3) mechanical disruption of secondary minerals present at mineral surfaces, and (4) release of less soluble colloids by dissolution of a more soluble matrix surrounding the colloids (Buddemeier and Hunt, 1988).

The mobility of colloids in the subsurface is controlled by the stability of the colloids in ground water, chemical interactions between colloids and immobile matrix surfaces, and hydrological and physical factors.

Particles can be removed by mechanical filtration through smaller pore spaces. Changes in aqueous chemistry can cause aggregation of colloidal particles or, if electrostatic and London-van der Waals forces are present, attachment to immobile surfaces (McDowell-Boyer and others, 1986). Colloids can be destabilized by increases in ionic strength, which result in compression of the double layer surrounding particles, by pH-induced changes in surface charge, or by the presence of strongly binding ions that decrease the net surface charge (McCarthy and Degueudre, 1993).

A significant problem in studying colloid mobility is ensuring that the colloids recovered from the wellbore are representative of conditions in the aquifer. Drilling redistributes material, creates fine particles, and introduces materials such as drilling mud. Sampling procedures can remove existing colloids attached to the immobile solid phase, create colloids during sampling, create colloids during separation from solution, or cause changes in the chemical and physical properties of natural colloids by altering the oxygen and carbon dioxide content, temperature, pH, Eh, and light as ground water is brought to the surface. Nucleation and precipitation of colloids on filter material can be mistakenly interpreted to indicate the presence of colloids in a water sample.

Colloids in ground water from proposed or existing nuclear waste sites have been measured. Up to 5 mg/L of colloids in water from fractured granites in Canada have been measured. They consisted of clay minerals, micas, quartz, feldspar, iron-silica oxides, and organic matter (Vilks and others, 1991). Naturally occurring colloids ranging in size from 0.050 to 1  $\mu\text{m}$  in ground water from fractures in the crystalline bedrock of the Grimsel site in Switzerland have also been measured (Smith and Degueudre, 1993).

### 4.5.2 Previous studies of actinide colloid formation and transport

Am, U, Np, and Pu oxides and hydroxides can exist as colloids in ground water (McCarthy and Degueudre, 1993). Evidence for association of actinides with colloids comes from laboratory batch and column experiments and field studies.

#### 4.5.2.1 Batch experiments

Formation of actinide colloids in laboratory experiments is dependent on the experimental conditions. The pH, concentration of complexing agents, including OH, CO<sub>3</sub>, PO<sub>4</sub>, SO<sub>4</sub> and F, and actinide concentration all affect whether colloids will form and at what rate. For aqueous

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solutions of actinides, polymers begin to form as pH increases. Increasing the pH of Pu and Am solutions with initial concentrations ranging from  $1 \times 10^{-7}$  to  $1 \times 10^{-11}$  M led to colloid formation at pH values between 7 and 9 (Ramsay, 1988).

Am solubility is smallest at a pH of 8. When Am stock solution was added to synthetic ground water, 80 percent of the Am was found to be in colloidal form; the colloids were between 0.008 and 0.450  $\mu\text{m}$  in size (Vilks and Drew, 1986). Colloid formation increased over a 4-day period before stabilizing. Geochemical modeling indicated that the solubility product for  $\text{AmOHCO}_3$  had been exceeded. In a similar experiment using saltwater, no Am colloids formed.

Adsorption of actinides by colloidal particles has been shown to affect calculated  $K_d$ s. Higgo and Rees (1986) found that Am, Np, and Pu  $K_d$  values decreased as ratios of solids to solutions increased. They attributed this behavior to increasing concentrations of colloids with adsorbed actinides moving through the 0.22- $\mu\text{m}$  filters that were used to separate the solid phase from the aqueous phase. Thus, the presence of actinides on colloids in the aqueous phase led to erroneously large solution concentrations and small  $K_d$  values.

Actinides have been shown to form colloid-sized complexes with organic molecules. Sheppard and Kittrick (1983) noted the presence of Am complexes with humic acids in the 0.001- to 0.010- $\mu\text{m}$  size range. Nelson and others (1985) determined that colloidal organic carbon and natural sediments used in laboratory experiments had approximately equal affinities for Pu (III+IV). Once complexed with the colloidal organic carbon, the Pu was mobile and unavailable for sorption by the natural sediments.

The association of actinides with organic carbon potentially can be an effective method for mobilization and transport from waste disposal sites. Organic material such as paper, cardboard, clothing, plastics, and other materials contaminated with radionuclides have been buried at the SDA (Humphrey and others, 1982). Vilks and others (1998) put compacted organic waste into airtight steel containers filled with water. After 18 months, the aged leachate contained 74 to 5,074 mg/L organic carbon and 5 to 110 mg/L of organic colloids. The leachate also contained large concentrations of Fe and Al, which could aggregate as colloidal particles.

Sheppard and others (1980b) measured U associated with colloidal humic molecules in the 0.001- to 0.010- $\mu\text{m}$  size range. These were batch experiments with soils. Sheppard and others (1980a) found evidence for U and Am complexes with large humic acid molecules (0.010 to

0.060  $\mu\text{m}$ ) in water from soils. Sheppard and others (1979) found evidence for Am and Np associated with a wide range of potentially mobile soil particles in the <0.001  $\mu\text{m}$  to 0.20  $\mu\text{m}$  size range.

##### 4.5.2.2 Column experiments

Colloidal transport of actinides in column experiments has been documented (Champ and others, 1982). Pu(IV) was applied as a spike to intact saturated-zone sand cores from the Chalk River Nuclear Laboratories, Ontario, and then eluted with uncontaminated ground water. Conditions were oxidizing; pH was 6.7, and  $\text{HCO}_3$  (9.5 mg/L),  $\text{SO}_4$  (18.5 mg/L), and Ca (6.1 mg/L) were the major ions. Small concentrations of Pu (mostly IV) were detected within 1 day of loading. The amount of Pu in column effluent increased gradually with time. At steady state, about 34 percent of the Pu in column effluent was associated with particulates (>0.450  $\mu\text{m}$ ), 16 percent was colloidal Pu (0.050 to 0.450  $\mu\text{m}$ ), 18 percent was 0.0028- to 0.050- $\mu\text{m}$  sized colloidal Pu, 28 percent was associated with a molecular weight between 500 and 10,000, and 6 percent was dissolved (<500 molecular weight). When columns were cooled to 0°C, the Pu release rate decreased fourfold within 48 hours. Upon reestablishing 22°C, 20 days were required to establish original equilibrium conditions. Release of Pu associated with both colloids and particulates was totally inhibited by antibiotic treatment. Release mechanisms were discussed by Champ and others (1982), but biologically mediated release of Pu is indicated by the data.

Seitz and others (1978) eluted Am and Pu through limestone, sandstone, and tuff columns. About 0.1 percent was eluted within a couple of pore volumes. Most of the Am(III) and Pu(IV) was concentrated near the inlet port of the column. Am(III) and Pu(IV) concentrations decreased exponentially along the column length. Transport could have been associated with a colloid or as discrete colloidal hydrolysis products.

##### 4.5.2.3 Field studies

Actinide colloids in ground water have been measured. Wastewater containing Am and Pu was disposed of in pits at Los Alamos National Laboratory in the 1940s and 1950s. Both Am and Pu in Mortandad Canyon, New Mex., several kilometers from the disposal sites, have been measured. Conductivity of ground water in this area ranges from 220 to 900  $\mu\text{S}/\text{cm}$ . The Am and Pu was associated with colloids having the same chemical composition as the soil matrix (Nuttall and others, 1991).

At a location 3.4 km from the disposal pits, Pu and part of the Am were associated with 0.0025- to 0.450- $\mu\text{m}$

sized colloids. About half of the Am was associated with a low molecular weight ( $<0.002 \mu\text{m}$ ) anionic complex of unidentified origin. Pu concentrations decreased exponentially along the flowpath. Am concentrations were variable (Penrose and others, 1990). The lithology of the disposal site is tuff, sand, silt, and clay derived from tuff. The researchers concluded that some Pu and Am could be transported by surface water during runoff events, but they stated that tritium oxide transit-time measurements indicated that most water movement took place in the subsurface.

Pu and Am colloids in the Bandelier Tuff beneath the former liquid waste disposal site at Los Alamos also have been measured. Laboratory studies found that essentially all Pu was retained within the top few millimeters of tuff core; however, in the aquifer 30 m below one disposal pit, Am and Pu concentrations as large as 5,000 Bq/kg were measured. In 1961, 20.5 m of additional water was added to this pit to change the distribution of radionuclides below the pits. Pu was found only 6.5 m below the bed, and Am was found 13.4 m (Nyhan and others, 1985).

About 5 percent of the U(VI) in ground water from the Koongarra deposit in Australia was associated with colloidal (defines as  $0.0015\text{--}1.0 \mu\text{m}$ ) kaolinite and silica (Payne and others, 1992). The remainder of the soluble U probably was transported as carbonate complexes.

### 4.5.3 Evidence for colloid-facilitated transport of actinides at the Idaho National Engineering and Environmental Laboratory

Transport of actinides associated with colloids in the subsurface at the SDA has not been proven conclusively. Results, however, from field sampling and laboratory column experiments indicate that colloid-facilitated transport of actinides could occur.

#### 4.5.3.1 Field evidence

Pu and Am in the subsurface at the INEEL have been measured. A memo from Jim Navratil to Doug Jorgensen, May 26, 1996, stated that Pu had migrated to the B-C and C-D interbeds. Possible transport mechanisms include formation of water-soluble organic or hydroxyfluoro complexes, or transport as colloids. Navratil and Jorgensen concluded that some of the reported detections of Pu were the result of analytical error or contamination.

Estes and McCurry (1994) showed that colloids are transported in the subsurface at the INEEL. Ground water was collected from USGS 45, USGS 46, and Site 14 using a straddle packer to isolate intervals. Ground water was filtered through  $0.45\text{-}$ ,  $0.20\text{-}$ ,  $0.010\text{-}$ , and  $0.02\text{-}\mu\text{m}$  mem-

brane filters. The water was supersaturated with respect to amorphous silica, calcite, and dolomite. Filters were analyzed by electron microscopy/energy dispersive X-ray spectroscopy (EDS) and point counting to determine concentration and composition. About 60 percent of the colloids were rounded and composed of Ca. About 5 percent were composed of ferrihydrite. Others were composed of Mg, Fe, Si, and Ca, and likely were clay. The authors suggested that some of the colloids could have been dislodged from fracture walls by pumping turbulence. Concentrations ranged from 2.1 to 1.8 mg/L for  $>0.45 \mu\text{m}$  in size, and 2.3 to 9.8 mg/L for  $<0.45 \mu\text{m}$  in size. For the 55- to 56-m depth, concentrations were 1.0, 2.7, and 6.1 mg/L for colloids of 0.20, 0.10, and  $0.02 \mu\text{m}$  sizes, respectively, and 1.2 mg/l for colloids between 0.45 and  $1.20 \mu\text{m}$ . Concentrations and size ranges of colloids in other depth intervals were similar to those in the 55- to 56-m depth. The results show that colloids exist in ground water at the INEEL; however, pumping dislodges some of the particulates attached to the fracture wall. This disturbance could skew measurements of the natural colloid concentrations. At one site, more than three borehole volumes were purged because initial water was brownish. Fractures and vesicles in basalt from beneath the SDA contain clay minerals and even some sand and silt (Right-mire and Lewis, 1987a); although the coarse material indicates transport of particles larger than colloids, it is likely that colloidal transport also occurs.

#### 4.5.3.2 Laboratory column experiments

Fjeld and others (1998) conducted column experiments to evaluate Pu(III+IV) and Pu(IV+V) transport in interbed sediments from the INEEL. The Pu was added to a synthetic perched ground water that contained potential complexing ligands. Batch distribution coefficient measurements indicated that Pu retardation by interbed material should be large; however, field measurements of Pu below the SDA suggested that Pu may have migrated through at least one interbed layer.

Column experiments were conducted by using interbed solids, both unwashed and washed, to remove colloids. A spike of Pu was added to the columns and then was eluted with uncontaminated ground water. The interbed material was composited from cores collected at five different depths ranging from 50 to 120 m and sieved to  $<250 \mu\text{m}$ . The interbed material was composed primarily of silt and clay. The synthetic ground water contained about 2000 mg/L of TDS, primarily Na,  $\text{CO}_3$ ,  $\text{SO}_4$ , and Cl, and 1.3 mg/L of humic acid, 1.3 mg/L of EDTA, and 20 mg/L of F.

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Columns were 8 cm long; inside diameters were 1.5 cm. Columns were dry-packed in 1 cm intervals by tapping to consolidate the sediment. One pore volume was 5.5 mL and the flow rate was 0.3 mL/min, equivalent to a linear velocity of 6.9 m/d. From 1,000 to 2,000 pore volumes of Pu-free water was eluted after the initial Pu spike was added.

Initial Pu concentrations were about 100 Bq/mL for Pu (III+IV) and 350 Bq/mL for Pu (IV+V). The washed columns were washed at a rate of 0.3 mL/min for 24 hours at pH 8, 24 hours at pH 10.7, 24 hours at pH 12, and 48 hours at pH 8.

In the Pu(IV+V) experiments, a small peak of Pu was eluted from the unwashed column when between 1 and 2 pore volumes had been eluted. The concentration of Pu that was eluted was about 0.07 percent of the initial spike concentration. For the washed columns, the effluent peak was 0.03 percent of the initial spike concentration. These peaks were followed by a nonzero residual for the remainder of the experiment. Total recovery was 4.3 percent for unwashed and 2.7 percent for washed columns. About 33 percent was Pu(IV) and about 71 percent was Pu(V).

In the Pu(III+IV) experiments, the concentration of Pu eluted from the unwashed columns when between 1 and 10 pore volumes had been eluted was steady at almost 2 orders of magnitude larger than background concentration. This was followed by a large peak that reached a maximum at between 20 and 1,000 pore volumes and had a retardation factor of 40. Total recovery was about 60 percent. The concentration of Pu eluted from the washed column when between 1 and 20 pore volumes had been eluted was steady at 1 order of magnitude larger than background concentration. This was followed by no detectable concentration from between 30 and 90 pore volumes, a broad peak that extended from between 100 and 1000 pore volumes, and a maximum concentration between 500 and 800 pore volumes. Total recovery was 16 percent. About 48 percent was Pu(IV) and about 51 percent was Pu(III).

Pu(IV+V) was more strongly sorbed than Pu(III+IV) and sorption was stronger in the washed columns. Approximately 90 percent of the sorbed Pu(IV+V) in the washed column was in the first 2 cm of the column. About 70 percent of the sorbed Pu(IV+V) in the unwashed column was in the first 2 cm of the column. About 55 percent of the Pu(III+IV) in the washed column was in the first 2 cm, and about 15 percent of the Pu(III+IV) in the unwashed column was in the first 2 cm.

Sr also was included in the initial spike. There was little difference in the Sr concentration profiles between unwashed and washed columns. A single peak of Sr was

eluted between 50 and 500 pore volumes. There was no evidence of a high-mobility fraction.

Results of these column experiments indicate the presence of multiple physical and chemical forms of Pu having different mobilities depending on the oxidation state of the Pu and the geohydrological history of the interbed. The implication of the results, if they accurately represent field conditions, is that transport models based on a single retardation factor calculated from batch distribution coefficient measurements may not accurately reflect actinide transport in the subsurface at the SDA. In the Pu(III+IV) experiments, there was a small, high-mobility fraction, a large, moderate-mobility fraction, and a large low-mobility fraction. In the Pu(IV+V) experiments there was more sorption, but also a small high-mobility fraction.

Possible mechanisms for Pu transport in these experiments include transport as an aqueous complex with F, CO<sub>3</sub>, EDTA, or humic acid, transport as a hydrolyzed solid, or transport as a sorbed phase on a mineral surface. The fact that more Pu(III+IV) was eluted from the unwashed column (60-percent recovery) than from the washed column (16-percent recovery) indicates that at least part of this fraction of Pu was associated with fine-grained minerals capable of being transported under these experimental conditions. Similar behavior would be expected for the Pu(IV+V) columns, yet there was only a small difference between the amount recovered from the unwashed (4.3 percent) and the washed (2.7 percent) columns. Additional data on the oxidation state of Pu in the column effluent could be used to quantify parameters for use in a solute transport model.

Newman and others (1995) also evaluated actinide transport in column experiments. Composite interbed sediment and crushed basalt were used. A spike of about one pore volume of synthetic ground water containing either Am, Pu(V), or U was added to the columns, and then 200 pore volumes of actinide-free ground water was eluted. The synthetic ground water used in these experiments was more dilute than the water used by Fjeld and others (1998). There was no added organic matter or EDTA, and F concentrations were only 0.5 mg/L. The columns were 15 cm long; inside diameters were 2.5 cm. Flow velocities were about 6 m/d.

There were peak concentrations of both Am and Pu when the first few pore volumes of all columns were eluted. The peaks for the coarser grained crushed basalt columns were much larger than those for the finer-grained sediment interbed columns. The Pu peak concentrations for the interbed columns were comparable to the Pu(IV+V) peak concentrations in interbed columns in

experiments by Fjeld and others (1998). There were no data to indicate whether Am and Pu were eluted from the columns as aqueous complexes or as colloids. In these experiments, materials that passed through a 0.2  $\mu\text{m}$  filter were considered.

The flow velocities used in these experiments were probably faster than expected velocities through the interbeds beneath the SDA. Other column experiments showed that decreasing column velocity decreased the size of the eluted actinide peak; however, the location of the peak did not change.

#### 4.5.4 Summary of colloid-facilitated transport of actinides

Evidence for the association of actinides with colloids comes from batch and column experiments and from field studies. Actinides are associated with a wide range of particle sizes, from the 500-molecular-weight range to clay sized and larger. They can exist as organic colloidal complexes and precipitates, and they can be sorbed by other minerals.

In laboratory column experiments, actinides eluted from columns packed with interbed sediments at a much faster rate than would be predicted from equilibrium sorption of aqueous species. This enhanced-mobility fraction was attributed to colloidal transport. The columns were relatively short; flow velocities through the columns were faster than expected velocities through the interbeds at the SDA but similar to expected velocities through fractured basalt. It is possible that actinide-bearing colloids migrating from the SDA could be mechanically filtered from suspension or removed by chemical or electrostatic forces. Better characterization of the colloids responsible for the enhanced breakthrough of Am and Pu observed in the column experiments is needed if this phenomenon is to be modeled. In addition, the percentage of actinides that could be associated with colloids and the percentage that could be in soluble complex form have not been determined.

The infilling of fractures and vesicles in the basalt beneath the SDA suggests the possibility of colloid transport; however, colloids at deep basalt intervals could have been transported from the surface or from interbeds immediately above the basalts. Colloids in fractures and vesicles also could have been emplaced as interbeds were forming.

One explanation for the occurrence of Pu in the B-C and C-D interbeds is that Pu mobility was enhanced by colloid transport. This explanation is consistent with both the strong association between Pu and colloids observed

in the laboratory and the evidence of the existence of colloids at the SDA. The occurrence of Pu in the B-C and C-D interbeds is also consistent with transport with small amounts of sorption. The small amount of sorption can be explained either by the formation of soluble complexes, notably  $\text{CO}_3^{2-}$ , or by slow sorption kinetics. Further study is needed to identify the geochemical characteristics of the subsurface water at the SDA, the sorption properties for the relevant variable geochemical conditions, and the geochemical and transport properties of the subsurface colloids.

#### 4.6 Summary

The purpose of this chapter is to determine what physical and geochemical processes might be invoked to explain observed detections. Generally, three factors are likely to affect actinide transport in the unsaturated and saturated zones near the SDA. These include preferential-flow mechanisms, the effects of redox conditions on actinide speciation, and colloidal transport of actinides. Because the sorptive characteristics of colloid-sized material are poorly understood and the formation of actinide-containing colloids is dependent on solution chemistry and redox conditions, it is difficult to evaluate colloidal transport of actinides at the SDA. Preferential flow and redox conditions are summarized in the following paragraphs.

The conceptual flow model as implemented in the numerical simulator assumes that infiltration beneath the surficial sediments is gravity driven and that the infiltration rates vary in space but are generally constant in time (Magnuson and Sondrup, 1998, p. 1-5). These assumptions do not account for transport of actinides outside the SDA boundaries under the relatively low infiltration fluxes that are applied at the land surface. The presence of  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  (undivided) in water from well D-15 (chapter 3, this report; S.O. Magnuson, LMITCO, oral commun., 1999) indicates that the preferential-flow mechanisms described in chapter 2 of this report that can cause local increases in flux can also affect contaminant transport. Lateral movement of water and contaminants would help explain the presence of contaminants of concern (COC's) outside the SDA boundaries. Lateral movement of water also would be consistent with the documented lateral movement of concrete grout for a distance of 168 m at the SDA (Rightmire and Lewis, 1987a, p. 64). It has been noted that there are gaps in the A-B and B-C interbeds beneath the SDA (chapter 2, this report). These interbed gaps could serve as drains for infiltrating water that has reached the basalt-interbed interface and moved



along the contact. The small number and seemingly random nature of radionuclide detections identified in chapter 3 of this report also indicate preferential flow in the subsurface at the SDA. These preferential-flow mechanisms add complexity to the geohydrologic system and to the computational scheme of the flow model, for example, extreme events such as flooding overwhelm the capacity of the system to transmit water through vertical fracture systems in the unsaturated zone. This incapacity forces lateral movement of water through horizontal fracture systems and could be the reason for the presence of COC's in the B-C interbed at well D-15, south of the western boundary of the SDA.

Generally, the ground water at the INEEL (and the SDA) is in oxidizing conditions: the ground water is saturated with DO and contains little organic carbon. At the SDA, a large amount of organic carbon (cardboard, wood, solvents, and other materials) and other waste was buried. As a result, it is likely that reducing conditions exist near the buried waste. These conditions will not persist indefinitely because the continual atmospheric supply of oxygen ultimately will consume all of the organic carbon associated with the waste. When this process is complete, oxidizing conditions will be reestablished. It is difficult to predict when this will occur. Am, U, Np, and Pu exist at the SDA in several different oxidation states. In this chapter, it has been shown that the transport and sorptive characteristics of these elements are affected by their oxidation state and by the redox conditions to which they are exposed. An important consideration when evaluating the mobility of these elements is whether current monitoring methods reflect long-term or transient conditions. It is possible that elements that are immobile in reducing conditions will convert to oxidation states that are mobile in oxidizing conditions. Hence, a change to oxidizing conditions could significantly affect actinide migration. For these reasons, it is necessary to have a good knowledge of the oxidation state of the COC's disposed of at the SDA and the oxidation state of any actinide detected at or near the SDA. Although the existing thermodynamic data sets are incomplete and inconsistent, surface complexation modeling techniques can help in evaluating actinide transport if the oxidation state of the element and redox conditions are known. Therefore, emphasis should be placed on identifying oxidation states and types of complexes or species formed by actinides detected at the SDA. This knowledge is necessary for the accurate prediction of actinide transport from buried waste at the SDA.

Magnuson and Sondrup (1998, section 5.4.1) discussed observed concentrations of  $^{241}\text{Am}$ ,  $^{238}\text{Pu}$ , and  $^{239,240}\text{Pu}$  in sediment from beneath disposal pit 2, the B-C

interbed, and the C-D interbed at the "triad" location, which includes wells TW-1, D-02, and 79-2 (located within 10 ft of each other in the north central part of the SDA). They compare the positive results at the B-C and C-D interbed depths to maximum model-predicted values at similar model locations and to the overall maximum values predicted by the model from all locations within the SDA. For the B-C and C-D depth intervals, the observed concentrations were 2 to 4 orders of magnitude greater than the predicted concentrations. The "triad" location is the only site in the SDA with concentrations in interbed samples larger than the minimum detection level (MDL) of  $5 \times 10^{-14}$  Ci/g established by the contractor's sample management office (SMO). They concluded that, because the "triad" samples were greater than predicted values, the model underestimated actinide migration at the SDA. However, they also concluded that, because of the lack of detections at other sites within the SDA, the model overpredicted migration at those sites. These conclusions seem contradictory and point out the weakness of using non-detection of actinides to confirm model predictions of values less than the MDL.

The fact that detections occurred in the subsurface at the "triad" location combined with the inability of the transport model to predict these detections indicates that there is a problem in the construction of the model. The failure of the model to predict these detections could be related to the assumptions in the conceptual model. For example, a single  $K_d$  was uniformly applied in the model. The  $K_d$  was derived from a laboratory experiment conducted on the fine-grained fraction of a composite sample using a synthetic liquid that was not representative of local water chemistry. It also was assumed that the interbeds were lithologically uniform, fine-grained material that was effective in retarding movement of contaminants. This is in spite of the limited knowledge about the characteristics and distribution of the interbeds.  $K_d$ s and their application to transport analysis is discussed extensively in chapter 5. The model may have underpredicted the actinide detections because (1) it does not adequately account for rapid movement of actinides past the interbeds by one or more of the preferential-flow mechanisms discussed in chapter 2, (2) the actinides may be in different forms resulting from different redox conditions in the source area and the area where the detections occur, or (3) the areal variability of actinide releases in the source area. The failure of the model to predict these detections indicates that significant characterization of the factors controlling actinide transport needs to be done. Particularly, data should be collected to adequately describe the variation in  $K_d$  resulting from differences in the areal distribu-



tion, thickness, and composition of the interbeds. The effects of preferential-flow mechanisms needs to be better understood. Understanding the form of the actinides is necessary to explain either their movement or lack of movement. Improving the understanding of these model variables should allow for better model predictions.

The fact that actinide measurements below the MDL occurred in all locations other than the "triad" location, and that the model predicted concentrations less than the MDL does not indicate that the model was successful in predicting actinide concentrations at those locations, it simply cannot be concluded one way or another. However, the inability to predict real detections at the "triad" location argues that the model cannot accurately predict actinide transport without a better understanding of the hydrologic system.

The occurrence of actinide concentrations larger than the MDL in the B-C and C-D interbeds at the "triad" location indicates that some form of transport is moving actinides from the SDA downward to the B-C and C-D interbeds at this location. The general decrease in  $^{238}\text{Pu}$  concentrations with depth from the B-C interbed to the C-D interbed (from  $1.18 \times 10^{-13}$  to  $3.22 \times 10^{-14}$  Ci/g) and for  $^{241}\text{Am}$  ( $8.40 \times 10^{-13}$  Ci/g) and  $^{239,240}\text{Pu}$  ( $1.07 \times 10^{-12}$  Ci/g) to less than the MDL also suggests that the B-C interbed may effectively retard the migration of actinides at the SDA. The migration of actinides to the B-C interbed and the reduced migration to the C-D interbed points out that some transport mechanism is active in this system and also that some retardation mechanism is active in the B-C interbed. In order to identify and evaluate these mechanisms further, it is necessary to enhance the database through additional data collection to define the continuity of the interbeds, their hydraulic properties, their mineral-

ogical composition, and their effect on transport of actinides in this system.

The uncertainties and complexities of actinide transport and the nonuniform distribution of actinides in the environment at the SDA limit use of the data from these detections in calibration of the model. As a result, the model was calibrated by using  $\text{NO}_3$ , which is considered to be a conservative indicator of transport in the system. The occurrence of a larger-than-background concentration of  $\text{NO}_3$  in water from well D-15 indicates both that  $\text{NO}_3$  can move in the unsaturated zone and that the preferential-flow mechanisms discussed in chapter 2 of this report probably operate at the SDA. However, the redox conditions near the SDA also can affect the stability of N compounds.  $\text{NO}_3$  is the stable form of N in an oxidizing environment; however,  $\text{NO}_2$  or  $\text{NH}_4$  generally is more stable in a reducing environment. If  $\text{NH}_4$  and  $\text{NO}_2$  were removed to an oxidizing environment that contained nitrifying bacteria, then a two-step nitrification process that first converted  $\text{NH}_4$  ion to  $\text{NO}_2$  and then  $\text{NO}_2$  to  $\text{NO}_3$  would take place. In this case, N would be conservative and could be used to determine longitudinal and transverse dispersivity. On the other hand, if nitrogen were present as  $\text{NO}_3$  in a reducing environment, it probably would undergo a N reduction process that converts  $\text{NO}_3$  and organic carbon to  $\text{CO}_2$  gas, water, hydroxide ion, and  $\text{N}_2$  gas. In this case, N would not be conservative and could not be used to determine dispersivity. Therefore, sample collection to determine the distribution of  $\text{NO}_3$  in the saturated and unsaturated zones should be expanded to include other forms of N. This would further substantiate the use of  $\text{NO}_3$  concentrations as a conservative indicator of the movement of wastes.

#### **4-28 Review of the transport of selected radionuclides in the Interim Risk Assessment**

## 5.0 Task 3: Distribution coefficients (K<sub>d</sub>s) and their application to transport analysis

### 5.1 Introduction

The fate and transport of waste constituents in geologic material are dependent on chemical and physical processes that govern the distribution of constituents between the solid, stationary phase and the aqueous, mobile phase. This distribution often is quantified by an empirically determined parameter called the Distribution Coefficient (K<sub>d</sub>). Many transport models for radionuclides use K<sub>d</sub>s to predict the extent to which the migration of the constituent will be lessened relative to the mean ground-water velocity. Although K<sub>d</sub>s are widely used, their application implicitly assumes that all factors affecting K<sub>d</sub>s are constant. However, these factors, which include pH, the concentration of competing adsorbates, the concentration of complexing ligands, and the availability and types of adsorption sites, generally are not constant in field environments such as the INEEL. Therefore, K<sub>d</sub>s may not adequately describe the transport and fate of waste constituents in some environments.

This section of the report evaluates the reliability of K<sub>d</sub>s and their application to transport analysis at the Subsurface Disposal Area (SDA), as described in the Interim Risk Assessment (IRA) (Becker and others, 1998). The evaluation includes a review of the literature on K<sub>d</sub>s that are specific to the SDA, as well as K<sub>d</sub>s reported for similar subsurface sediments elsewhere. The K<sub>d</sub>s are evaluated in terms of the existing subsurface mineralogy and aqueous geochemical conditions. The experimentally determined K<sub>d</sub>s for Am, U, and Pu used in the IRA model are discussed in section 5.3, and the K<sub>d</sub>s for Np from previous studies are evaluated in section 5.4.

This evaluation specifically considers the K<sub>d</sub>s used for Am, U, Np, and Pu, the experimental protocols used to determine the K<sub>d</sub>s, and the adjustment of the reported K<sub>d</sub>s to account for site-specific conditions such as the presence of carbonate from caliche layers. This evaluation also examines the extent to which the K<sub>d</sub> concept may be applicable to the SDA, as well as the uncertainty associated with the K<sub>d</sub>s used for fate and transport modeling. Many factors contribute to the uncertainty, including extrapolation of the laboratory-derived K<sub>d</sub>s to field conditions and the effects of spatial variability of the sorbing phases.

### 5.2 Literature review

The actinides comprise the series of radioactive elements from actinium (atomic number 89) to lawrencium (atomic number 103). Of specific interest at the SDA are Am, U, Np, and Pu. The dominant species of these elements in ground-water systems are given in table 5-1.

Table 5-1 Important (\*) and usually unimportant (\*\*) oxidation states of some actinides in natural rock-water systems (from Langmuir, 1997)

Actinide charge	Actinide cation (An)	Element/atomic number			
		U/92	Np/93	Pu/94	Am/95
6+ (VI)	AnO <sub>2</sub> <sup>2+</sup>	*	**	*	
5+ (V)	AnO <sub>2</sub> <sup>+</sup>	**	*	*	
4+ (IV)	An <sup>4+</sup>	*	*	*	
3+ (III)	An <sup>3+</sup>		**	*	*

#### 5.2.1 K<sub>d</sub> basics

"K<sub>d</sub> or not K<sub>d</sub>, that is the question." (Rancon, 1986).

K<sub>d</sub>s for radionuclides on earth materials have been measured and used in environmental assessments at nuclear facilities since the early days of operations at these sites. The number of measurements has been described by Bror Jensen (1982) of Riso National Laboratory, Denmark, as "almost incalculable." The applicability and limitations of the K<sub>d</sub> concept will be introduced here.

Sorption processes can be studied in the laboratory by a batch method. This involves adding a known quantity of sorbate (for example, a radionuclide) to a system containing a known quantity of sorbent (for example, soil, rock). After equilibration at constant temperature, the quantity of sorbate on the solid, and that remaining in solution are measured. The initial solution concentration is varied and the equilibration and analysis process is repeated. Sorption isotherms are plots of the quantity of sorbate on a solid sorbent per unit weight of sorbent (pCi/g), versus the equilibrium solution concentration of the sorbate (pCi/mL). A typical sorption isotherm for a trace solute sorbing onto a solid is shown in figure 5-1. The maximum percentage of the solute is sorbed at the smallest sorbate concentration. A tangent drawn to the steep, initial portion of this empirical curve gives the ratio of the amount sorbed to the concentration in solution. This slope has

## 5-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

been designated as the "distribution coefficient,"  $K_d$  (Langmuir and Mahoney, 1984) (equation 4.1). Measured  $K_d$ s are typically reported in units of mL/g or L/kg. A non-reactive sorbate will have a  $K_d$  near 0; a reactive sorbate may have a  $K_d$  of  $10^2$  to  $10^3$  or larger.

The larger the  $K_d$ , the greater the retardation of the solute. This is reflected in the retardation factor,  $R_F$  (equations 4.2 and 4.4). In laboratory column experiments where  $R_F$  is measured,  $K_d$  may be calculated by the equations above. The column method represents an alternative to the batch technique. Although the column method is more labor intensive than the batch method, it does allow for the identification of species of differing mobilities, for example, a "fast fraction," that otherwise may be lumped in the batch method.

Distribution coefficients are typically normalized on a per unit weight of sorbent basis. However, they also may be normalized on a per-unit-of-surface-area basis ( $\text{mL/m}^2$ ). The distribution coefficient in terms of surface area,  $K_a$ , is related to the more commonly used  $K_d$  by:

$$K_a = \frac{K_d}{S_A} \quad (5.1)$$

where:

$S_A$  = specific surface area of the sorbing phase (a mineral, soil, crushed rock or any porous medium), in area per mass.

Bertetti and others (1998) have shown how surface-area measurements, as a relative measure of the number of sorption sites on a mineral surface, can be used to compare the Np(V)-sorbing properties of different materials. Whereas the  $K_d$  data in figure 5-2a suggest differing sorption properties between two types of quartz and alumina powders, normalization to surface area (fig. 5-2b) showed similar  $K_a$ s. Similar findings for U(VI) sorption on a variety of minerals have been reported by Pabalan and others (1998). Although montmorillonite  $K_d$ s over a pH range of 2 to 9 are as much as an order of magnitude larger than those for the zeolite mineral clinoptilolite, their  $K_a$ s are almost identical. For fractured media,  $K_a$  can be used in modeling the sorption of contaminants. For uncoated fractures, an estimate of the surface area of the fracture walls would be used. However, Rightmire and Lewis (1987a) have shown that many of the basalt fractures in the unsaturated zone at the SDA are coated or filled with clays, iron-stained quartz sand, calcium carbonate, and other fine-grained materials. In modeling the sorption of contaminants in these fractures, Magnuson and Sondrup (1998, p. 5-2 to 5-6) used the specific surface area of the material coating the fracture in the  $K_a$  term; extrapolating

from surficial sediment data from the SDA, this value was  $20 \text{ m}^2/\text{g}$ .

The  $K_d$  determined for a given constituent in the laboratory is unique to the solution properties (pH, competing ions, complexing ligands, etc.), and sorbent properties (mineralogy, organic matter content and character, surface area, etc.) being investigated. The  $K_d$  may vary with the method used to determine it—batch, column, or *in situ*—as well as with intramethod variations, such as the solid:solution ratio in batch experiments, flow rates in column experiments, and particle-size fractions measured for *in situ* experiments. Caution is necessary when results from laboratory experiments are extrapolated to field conditions. Where solution composition is variable, for example, in a contaminated ground-water system, solute transport modeling based on a single  $K_d$  may have inherent problems. Despite these limitations,  $K_d$ -based solute transport modeling has been widely used in the study of organic, inorganic, and radioactive contaminants in the subsurface (Freeze and Cherry, 1979).

*In situ* measurements of  $K_d$  are rare but intrinsically appealing, because sorption has occurred under field conditions. Some investigators have determined *in situ*  $K_d$  by measuring the ratio of the concentration of the radionuclide of interest in the sampled soil or rock interval, to the concentration in the sampled ground water. *In situ* measurements have included  $K_d$ s for  $^{239,240}\text{Pu}$  at Enewetak Atoll (Noshkin and others, 1976), and for  $^{60}\text{Co}$ ,  $^{106}\text{Ru}$ , and  $^{125}\text{Sb}$  at an unnamed low-level radioactive waste disposal site (Fruchter and others, 1985). Other investigators have approached the issue of  $K_d$ s for selected transuranic elements and fission products by measuring analog radionuclides associated with natural decay series (natural analog studies). For example, U(VI) can be used as an analog for Pu(VI), and Th(IV) can be used as an analog for Pu(IV) and Np(IV). Two approaches have been used for *in situ*  $K_d$  measurement. One involves measurement of only the solute phase (Krishnaswami and others, 1982). The other involves measurement of both solid and aqueous phases, in some cases using selective extractants to identify sorbed radionuclides. There has been considerable dialog on the uses and abuses of natural analog studies in assessments of radionuclide migration (McKinley and Alexander, 1993; Ivanovich, 1993). Investigators at Los Alamos National Laboratory, the University of Southern California, and the INEEL indicate that U-series and Th-series isotopes (in an approach which appears to be similar to that of Krishnaswami and others, 1982) in the Snake River Plain (SRP) aquifer are being investigated as natural analogs of contaminant transport at the

INEEL (Luo and others, 1998; Roback and others, 1998). Details of these applications are not yet available.

K<sub>d</sub>s generally imply retention by ion adsorption reactions—ion exchange or specific sorption—retention by the solid surface based upon its surface charge. However, solutes can be removed from solution by other processes, such as precipitation and coprecipitation, where new bulk solid phases are formed (Sposito, 1984). For example, in comparing trace metal binding constants (distribution coefficients normalized by density of exchangeable surface sites) in surficial ocean sediments from different basins, investigators excluded Mn, Fe, and Ba from consideration in sediments where enrichment appeared to be due to the formation of Mn and Fe oxides and BaSO<sub>4</sub>, rather than to adsorption (Balistrieri and Murray 1984). The K<sub>d</sub>s determined when an acidic, radionuclide-bearing solution comes in contact with a calcareous soil horizon may reflect the combined effects of adsorption, coprecipitation, and/or precipitation onto and in freshly precipitated Fe(III), Al, and Mn(IV) oxyhydroxides, as well as ion exchange reactions with clay minerals. Langmuir (1997, p. 356–357) refers to these as “lumped-process” or “apparent” K<sub>d</sub>s, and presents an example of laboratory neutralization of a Th-bearing water by CaCO<sub>3</sub> to demonstrate the nonlinear variation in apparent K<sub>d</sub>s from about 2 at pH 2 to about 15,000 at pH 8. These K<sub>d</sub>s are system specific, and have limited transfer value to other systems having different conditions or compositions.

## 5.2.2 Sorption processes

Experimental sorption data typically are described by empirical measures such as K<sub>d</sub>. Such empirical measures provide little information on the mechanism of sorption and are highly dependent on temporal and spatial variations in the chemical composition of the aqueous phase and in the nature and properties of the sorbing solids. Desiring a means to describe sorption in a general geochemical framework of changing water chemistry and nonuniform mineralogies, investigators have developed Surface Complexation Models (SCMs) that describe reactions between functional groups on mineral surfaces and soluble species identified by aqueous speciation models (Davis and Kent, 1990). Such SCMs have been developed to describe U(VI) sorption on ferrihydrite (Waite and others, 1994), quartz (Kohler and others, 1996), kaolinite (Turner and Sassman, 1996), and montmorillonite (Pabalan and Turner, 1997). SCMs have been used to simulate Np(V) sorption on montmorillonite (Tsukamoto and others, 1997; Turner and others, 1998), gibbsite (Del Nero and others, 1997), hematite (Kohler and others, 1999),

and magnetite and goethite (Fujita and others, 1995). Turner (1995) reviewed additional studies on actinides, including the use of SCMs to simulate the sorption of Am(III) on alumina and amorphous SiO<sub>2</sub>, and Pu(IV, V) on alumina and goethite. Most SCM investigations have focused on monomineralic systems. Recent work by Davis and others (1998) extended the application of the surface complexation concept to complex mineral assemblages, in this case, Zn<sup>2+</sup> sorption by an outwash sand, aquifer material from Cape Cod, Mass. With continued progress in the development of such models to address complex geochemical environments, in the future these models could be coupled with reactive-transport codes and used as the method of choice in performance assessment simulations of radionuclide migration at nuclear waste sites. However, currently, transport calculations used in these assessments continue to rely on empirical sorption coefficients, principally K<sub>d</sub> (Vandergraaf and others, 1993; Turner, 1995).

As previously noted, many experimental factors can influence K<sub>d</sub> determinations. These include:

- pH,
- Eh,
- speciation of sorbate,
- concentration of complexing or competing solutes,
- solid:solution ratio and method of phase separation at the end of an experiment,
- radionuclide concentration,
- adsorption versus desorption measurements,
- time,
- temperature, and
- properties of the sorbent, including particle size.

The thousands of batch K<sub>d</sub>s in the literature have been determined by many laboratories, each with its own procedure. These procedures often are not well documented in the reports. Several standardized procedures have been developed for batch K<sub>d</sub> measurements (American Society for Testing and Materials, 1987, 1993; Relyea and others, 1980). The standard batch K<sub>d</sub> procedure of Relyea and coworkers at Pacific Northwest National Laboratory (PNNL) (1980, appendices A and B) was developed for Department of Energy's (DOE) Office of Nuclear Waste Isolation as part of the Waste/Rock Interaction Technology (WRIT) Program. The procedure is highly detailed and contains information of specific value in radionuclide K<sub>d</sub> measurements; for example, cautions on preparation and addition of tracer to ground water. This program also has produced recommendations on column methods for K<sub>d</sub> measurement (Relyea and others, 1980, appendix C; Relyea, 1982). The latter report contains specific recommendations on water velocity and column dimensions.

## 5-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

One of the goals of the WRIT Program was to produce a critically reviewed data base of  $K_d$  values for a suite of long-lived radionuclides on rocks, sediments, and minerals at candidate repository sites over a wide range of ground-water compositions (Serne and Relyea, 1981). This data base effort has not been sustained at PNNL. In recent years, there has been a strong push in the performance assessment community for reliance on site-specific  $K_d$ s, rather than literature-derived values (Krupka and others, 1999; Kaplan and Serne, 2000).

### 5.2.2.1 Alternatives to single $K_d$ values

It is apparent that with all of the experimental variables noted above that can influence a  $K_d$  determination, and with the field-scale spatial variability in sorptive properties of earth materials, it is difficult to characterize a complex and dynamic transport system with a single  $K_d$  value. Investigators have suggested various means to deal with this problem:

- Turner (1995) has suggested using surface complexation models to assess the effect of critical system properties (for example, pH) for conditions beyond the range used in the sorption experiments. The calculated sorbed and aqueous-phase concentrations can be used to generate a range of  $K_d$  values predicted as a function of these variables. The range of  $K_d$ s thus developed can then be used in transport calculations to bound the simulation, rather than assuming a single case.

- Serne and Relyea (1981) considered the inability of the batch method to differentiate multiple species of a radionuclide as this method's major limitation. They recommended using at least two methods (for example, batch and column) in concert to bound radionuclide migration assessments. Such a combined approach has been used by Triay and others (1996) in evaluating sorption retardation of Np by the Yucca Mountain tuffs.

- Vandergraaf and others (1993) consider the effects of variables such as changes in mineralogy and ground-water composition on  $K_d$ s for given flowpath segments.

### 5.2.2.2 Importance of secondary minerals

Many lines of evidence testify as to the importance of iron ( $\text{Fe}^{3+}$ ) oxides and manganese oxides as host phases for trace metals and radionuclides in undisturbed and disturbed earth materials. Many examples of this evidence are described in a report by Jenne (1998a). In summarizing priorities for future metal and radionuclide adsorption research, Everett Jenne of PNNL noted (Jenne, 1998b; p. 551): "Iron oxides are nearly always an important adsorbent in natural systems and, except for reducing conditions or the case where the Fe oxide concentration is low

or another adsorbent is relatively high, they are the dominant adsorbent."

One of the earliest investigations highlighting the importance of such phases in radionuclide retention examined soils at the solid- and liquid-radioactive waste burial grounds at Oak Ridge National Laboratory (Means and others, 1978b). Using selective extraction procedures, the investigators showed that  $^{60}\text{Co}$ ,  $^{244}\text{Cm}$ ,  $^{241}\text{Am}$ , and  $^{238}\text{Pu}$  (lumped) were associated predominantly with Mn oxides. The linear correlation coefficients between radionuclide concentrations and Mn oxide contents in selected soil samples ranged from 0.67 ( $^{244}\text{Cm}$ ) to 0.94 ( $^{60}\text{Co}$ ). For the same soils, the correlation coefficients between these radionuclides and Fe oxide content ranged from 0.12 ( $^{60}\text{Co}$ ) to 0.50 ( $^{241}\text{Am}$  and  $^{238}\text{Pu}$ ). The dominant association with the Mn oxides occurred despite the fact that the Fe oxides were present at concentrations 2 to 30 times that of the Mn oxides. Like the Mn oxides, most of the Fe oxides are poorly crystalline (amorphous by X-ray diffraction). In contrast, work by Fruchter and others (1985) on alluvial sediments from the 100 N Area low-level radioactive waste disposal site at the Hanford Reservation suggested that amorphous iron oxides were the dominant sorbing phase for  $\text{NpO}_2^+$  [ $\text{Np(V)}$ ]. Np sorption increased as the amorphous Fe oxide content of the sediments increased. Evidence suggested that Mn oxides, occurring in small concentrations in these sediments, were a lesser factor in determining the extent and pH dependence of Np sorption in this system.

The presence of Fe oxides in the weathered basalts and interbeds at the INEEL often has been reported in qualitative terms. Ferrihydrite (or other unspecified Fe-bearing minerals) and Fe oxyhydroxides have been reported to be present as fracture-filling material in basalts and in the interbeds at the Idaho Nuclear Technology and Engineering Center (INTEC, formerly the Idaho Chemical Processing Plant (ICPP)) and the SDA (Estes and McCurry, 1994; Rightmire and Lewis, 1987a). Jorgensen and others (1994) noted that the reddish brown color of the A-B interbed was due to the oxidation of Fe-rich minerals, and that basalt pebbles with Fe-filled vesicles were present in the B-C interbed. Although the presence of these oxide phases has been noted, their quantitative assay and characterization in basalts, fracture fillings, and interbed sediments at the INEEL has been very limited.

Much attention has focused on bulk mineralogic analyses by X-ray diffraction (XRD) (Barraclough and others, 1976, Table A-V; Rightmire and Lewis, 1987b, table 7). In this latter example, Fe oxyhydroxides were, in some cases, removed from interbed sediment samples

from the SDA by a dithionite-citrate extraction (a standard pretreatment for XRD analysis of clay minerals). This treatment also extracts Si, Al, and Mn oxides (Jackson and others, 1986). Such treatments have been used routinely in soil and sediment XRD analysis to decrease fluorescence by the Fe oxides, and thereby improve the quality of the XRD patterns. Analysis of the extract solution for Fe and other oxide constituents can potentially quantify and characterize important radionuclide sorbents in the system. Rosentreter and others (1998) investigated U sorption on sediments from the Delmarva Peninsula in Virginia. Among the mineralogic characteristics of the sediments examined were bulk mineralogy (by optical microscopy), surface area, dithionite-citrate extractable Fe, and oxalate extractable Al. No correlation was observed between K<sub>d</sub>s and bulk mineralogic parameters (for example, percent plagioclase feldspar). U K<sub>d</sub>s were strongly correlated with surface area. Measured surface areas were strongly correlated with amounts of hydrous oxide coatings on the sediment (as measured by extractable Fe + Al). K<sub>d</sub>s could be predicted by a linear regression equation combining pH with either surface area or extractable metals content. Rosentreter and others (1998) noted the importance of characterizing the spatial variability of surface area, even at sites that appeared to be mineralogically homogeneous, when attempting to describe reactive properties such as K<sub>d</sub>. Although attention tends to focus on the Fe oxides, the surface complexation properties of Fe and Al oxides are similar, and clay minerals with pH-dependent charge sites are assumed to have surface characteristics similar to these oxides (Bradbury and Baeyens, 1993). Such pH-dependent charge sites on clay minerals are in addition to permanent charge sites that play a major role in the retention of cationic species. Future sorbent characterization research at the INEEL would benefit by focusing on secondary minerals, particularly oxides and clay minerals.

New surface spectroscopic techniques may yield information on surface species and important sorbent phases that can be useful in the development of SCMs to simulate actinide retention. For example, Duff and others (1999a) used X-ray absorption spectroscopy, in combination with microautoradiography, electron microprobe, and petrographic microscopy techniques to study the bonding environment of Pu on the zeolitic Topopah Spring Tuff sampled at Yucca Mountain. Thin sections of the tuff from the 450-m interval were exposed to a synthetic ground water spiked with Pu(V). Large concentrations of sorbed Pu were associated with smectite and Mn oxide fracture minerals. Sorption of Pu to Fe-rich regions was not observed. Both Pu(V) and Pu(VI) were observed as

sorbed species, indicating that heterogeneity is an issue in terms of Pu oxidation at the surface (Duff and others, 1999a, 1999b). In a similar experiment in which a devitrified sample from the Prow Pass Tuff was used, Pu was concentrated in the zones of altered orthopyroxenes; these zones contained amphiboles and Fe-rich amorphous materials (Vaniman and others, 1996). Reduction of Np(V) to Np(IV) at mineral surfaces in granites has been postulated as an explanation for unexpectedly large K<sub>d</sub>s (Hadermann and Gunten, 1988); X-ray absorption spectroscopy appears to be a tool to address such questions.

CaCO<sub>3</sub> fills fractures and vesicles in many unsaturated zone cores from near the SDA (Rightmire and Lewis, 1987a) and has been observed to sorb U (Milton and Brown, 1987; Baudin and others, 1988), Np(V) (Morse and Choppin, 1991), and Am (Higgo and others, 1986). Rawson and others (1991) suggested that Am may be preferentially sorbed with respect to Pu or coprecipitated in calcareous surficial and interbed sediments at the SDA. Follow-up mineralogic work to investigate this possibility was noted as planned; the status of such work is currently (1999) unknown.

#### 5.2.2.3 Role of Fe<sup>2+</sup>-bearing minerals

The basalts and interbed sediments at the SDA contain Fe<sup>2+</sup>-bearing minerals. The basalts contain pyroxenes and olivine as major mineral phases and magnetite as an accessory mineral (Knutson and others, 1990). The interbed sediments contain pyroxenes (predominantly augite) and olivine (Bartholomay, 1990b, 1990c). Bondietti and Francis (1979) first reported the reduction of the relatively mobile species NpO<sub>2</sub><sup>+</sup> [Np(V)] to a less soluble form (probably NpO<sub>2</sub> [Np(IV)] or related hydrated phase) by contact with various granites and basalts. The results of laboratory experiments, performed under O<sub>2</sub>-free conditions, are shown in figure 5-3. That this removal from solution by the igneous rocks was associated with reduction to Np(IV) rather than sorption of Np(V), was demonstrated by extraction from the rock, followed by a separation of Np(IV) from Np(V) by precipitation with zirconium phenylarsonate. Experiments in which Pu(V) was used as the starting species showed rapid reduction to Pu(IV) by basalts, granites, and unweathered shales. These latter rocks did not reduce Np(V). Work by Meyer and others (1985) on Np(V) reduction and retention by the Umtanum Basalt from the Hanford site showed that about 90 percent of the sorbed Np was present as Np(IV), whether the system was oxic or anoxic. This suggests that the process could be operative at ferrous mineral surfaces in contact with the oxygenated ground water of the SDA subsurface environment. With prolonged oxidation of

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basalt surfaces by oxygenated water, all the accessible reactive ferrous iron components of the basalt likely will be oxidized, thus decreasing the impact of the retention mechanism.

Bondietti and Francis (1979) showed that pretreatment of the Sentinel Gap Basalt (sampled north of the Hanford Reservation) with sodium hypochlorite (to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ) decreased the removal of Np from solution. The pretreated oxidized basalt showed essentially no Np reduction. The removal of Np from solution by the oxidized basalt may represent sorption of Np(V) by ferric oxyhydroxides formed at ferrous mineral surfaces by the oxidizing action of the sodium hypochlorite. Column experiments in which fractured cores of unaltered and artificially, hydrothermally-altered basalts from the Hanford site showed far greater retention of Pu and Np by the unaltered basalts (Vandegrift and others, 1984). If retention of the radionuclides in the unaltered basalts is due to reduction by ferrous iron, then the lesser retention in the hydrothermally-altered basalts may reflect adsorption by ferric oxyhydroxides formed at mafic mineral surfaces during the autoclaving procedure used to alter the basalts. Petrographic descriptions done as part of the vadose-zone basalt characterization (Knutson and others, 1990) demonstrate that flow tops (and sometimes flow bottoms) are generally oxidized, showing a reddish or orange color that may penetrate about 1 m below the flow surface. On crystal faces and along grain-fracture surfaces of olivine grains there are often brassy-appearing, surface oxidation layers. Locally, oxidation of entire olivine grains may occur.

The possible reduction of actinides by mineral-bound ferrous iron received considerable attention in the Basalt Waste Isolation Program (BWIP) as a possible retardation mechanism. The preceding discussion suggests that its importance *in situ* may be lessened by oxidation of ferrous iron in water-bearing fracture and interbed zones. Its importance in the interbed sediments and basalt fracture zones at the INEEL has yet to be investigated. This geochemical process also should be considered when fresh basalts have been ground and used for  $K_d$  determinations.

Besides  $\text{Fe}^{2+}$ , other possible reductants for actinides in the subsurface environment include naturally occurring and synthetic organic substances (Bondietti and Sweeton, 1977; Cleveland and Mullin, 1993). The speciation of Am and Pu in ground water at the SDA was investigated by Cleveland and Mullin (1993). They found that water from a perched zone at 65 m sampled at well USGS 92 within the SDA had a greater ability to retain Pu, added as a soluble, reduced [Pu(III), Pu(IV)] spike, in solution than did

any of the other water samples tested. Pu(IV) is probably the dominant Pu form in the waste buried at the SDA (Rightmire and Lewis, 1999). It also was the dominant species identified in ground water sampled at well USGS 40 near the ICPP disposal well (Rees and Cleveland, 1982). Reduction of a major fraction of the Pu(IV) to the more soluble Pu(III) oxidation state was demonstrated in these laboratory studies. Cleveland and Mullin (1993) suggested that the enhanced solubility of Pu in water from well USGS 92 was due to the reducing action of dissolved organic compounds and inorganic complexation by carbonate ions.

### 5.224 Influence of organic compounds on subsurface migration of actinides

Organic compounds can form complexes with actinides, which can influence both the solubility and sorption behavior of these radionuclides. The organic compounds may be naturally occurring (for example, humic and fulvic acids) or may be organic materials disposed of in the waste such as ethylenediaminetetraacetic acid (EDTA). The latter class includes degradation products of organic materials in the waste (for example, organic acids produced by the decay of cellulose).

Early work on the complexation of radionuclides by humic substances in water has been reviewed by Boggs and others (1985). The mobility of actinides may be decreased in situations where these radionuclides bind to insoluble humic materials (Boggs and others, 1985). The formation of soluble complexes may enhance transport. Figure 5-4 shows a strong inverse relation between the  $K_d$  for Np sorption onto basalt from synthetic ground water and the concentration of dissolved humic acid (a similar pattern was seen with Am). A strong inverse relation between actinide  $K_d$ s and dissolved organic carbon (DOC) has been observed in other geochemical environments—for example, in lake water receiving fallout-derived Am and Pu(III, IV) (Nelson and Orlandini, 1986). Cochrane and others (1996) showed that photo-oxidation of organic carbon in the DOC rich water of the Ob River (Russia) increased  $K_d$ s for  $^{241}\text{Am}$  on river sediments by one to two orders of magnitude.

Recent studies by McCarthy and others (1998a, 1998b) suggest that natural organic matter may play a key role in the rapid ground-water transport of  $^{241}\text{Am}$  and other actinides from shallow, unlined disposal trenches in fractured-shale saprolite at Oak Ridge National Laboratory. The saprolite at the Oak Ridge National Laboratory is high in clay minerals, calcite cements, and amorphous Fe- and Mn-oxides, and was expected to sorb the actinides;  $K_d$  for  $^{241}\text{Am}$  from synthetic ground water in



the absence of natural organic matter was 8,900 dm<sup>3</sup>/kg. DOC (<1 nm in filtrate) in the shallow (8 m) ground water at the Oak Ridge site ranged from 0.45 to 0.69 mg/L (total organic carbon (TOC) in unfiltered samples ranged from 0.5 to 0.75 mg/L) (McCarthy and others, 1998a). To compare these ranges with those of ground water at the INEEL, Leenheer and Bagby (1982) reported on 77 DOC (< 0.45  $\mu$ m filtrate) measurements from across the site, including wells at or near the SDA. DOC was 8.7 mg/L in well USGS 92 (depth, 64 m) and ranged from 1.6 to 8.7 mg/L in four SRP aquifer wells (USGS 87 through 90). DOC ranged from 3.3 to 13 mg/L in 10 wells monitoring background SRP aquifer water, remote from the INEEL processing or waste inputs. DOC ranged from 0.3 to 0.7 mg/L in eight SRP aquifer wells (USGS 87 through 90, USGS 117, 119, 120, and RWMC Production), listed in table 14 of Knobel and others (1992b). DOC was 0.8 mg/L in the Big Lost River (BLR) when measured on 19 November 1998. The nature of the DOC at the SDA and its ability to form stable actinide complexes needs to be investigated before the relative importance of this process in actinide migration at the site can be assessed.

The role of synthetic organic compounds in complexing and mobilizing radionuclides in shallow landfills was first reported by Means and others (1978a) for <sup>60</sup>Co at an intermediate-level liquid waste burial ground at Oak Ridge. This work focused on EDTA, a nonvolatile organic compound that has been specifically monitored at the SDA (Knobel and others, 1992a; Jorgensen and others, 1994). Monitoring for this compound is perhaps due to information received from the waste generators. However, many other complexants are used in decontamination and other operations in the nuclear industry. These include diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), and citric and oxalic acids (Boggs and others, 1985). Delegard and others (1984) noted that EDTA and HEDTA decreased the sorption of the radionuclides Sr, Np, Pu, and Am on Hanford sediments; HEDTA decreased sorption of <sup>60</sup>Co, but EDTA increased it. This latter result is seemingly in contrast to the earlier findings at Oak Ridge by Means and others (1978a). The extreme complexity of the sorption of Co(EDTA)<sup>2-</sup> on Fe- and Mn-coated subsurface materials such as those at Oak Ridge, Hanford, and the INEEL, has been studied by Zachara and others (1995). The sorptive behavior of Co was shown to be linked to the oxidation of Co<sup>2+</sup>(EDTA)<sup>2-</sup> to Co<sup>3+</sup>(EDTA)<sup>1-</sup> by Mn oxides in the subsurface materials, and the subsequent sorption of these different complexes by the Fe and Mn coated surfaces.

In addition to process reagents such as EDTA, organic wastes at disposal sites can contain a wide variety of materials such as plastics, rubber, paper, ion-exchange resins, and solvents. Chemical and biological degradation of these materials can release compounds that can influence actinide sorption. Cellulose materials have received considerable attention due to the large quantities of wood and cardboard used in waste packaging and rags and clothing used in decontamination. Leachates from the alkaline degradation of cellulose (as might occur in a cement matrix) were found to decrease the sorption of Pu onto cement by about two orders of magnitude. The decrease in Pu sorption is believed to be due to strong complexation of the Pu by hydroxyl groups present in compounds such as isosaccharinic acids, which result from the alkaline degradation of cellulose (Greenfield and others, 1992). Although the preceding discussion has focused on sorption for some waste disposal scenarios, organic complexes from cellulose degradation may have a more important effect on solubility of actinides than do the carbonate complexes more typically modeled during the early period following disposal (Stockman, 1998).

### 5.3 Evaluation of the K<sub>d</sub>s for Am, U, and Pu used in the Interim Risk Assessment model—experimental data

The purpose of this section is to evaluate the K<sub>d</sub>s selected and applied to the IRA for Waste Area Group 7 (WAG-7) given the known, site-specific information. K<sub>d</sub>s used in the IRA model (Becker and others, 1998) were selected from those reported by Dicke (1997). These K<sub>d</sub>s were determined to be the most appropriate for fate and transport modeling at this site. The intent was to maintain conservatism in the transport simulations by selecting the lowest values from a range of K<sub>d</sub>s. This was done for Am and Pu. For U and Np, intermediate K<sub>d</sub>s were used. K<sub>d</sub>s for Am, U, and Pu were determined experimentally using aquifer solids from the INEEL and synthetic ground water similar in chemical composition to that from the SRP aquifer (Newman and others, 1995). K<sub>d</sub>s for Np were selected from the literature. In this review, site-specific K<sub>d</sub>s for Am, U, and Pu are evaluated first, followed by a discussion of the Np K<sub>d</sub>s.

K<sub>d</sub>s for Am, U, and Pu, reported by Dicke (1997), are based on results from batch and column experiments conducted by Goff (1994) and Newman and others (1995). Table 5-2 summarizes the K<sub>d</sub>s in these experiments. For the interbed sediments, Dicke (1997) recommended that K<sub>d</sub>s of 450 mL/g for Am, 6 mL/g for U, and 5,100 mL/g for Pu, be used in the IRA model. K<sub>d</sub>s of 225 mL/g and 900 mL/g for Am, 9 mL/g for U, and 3 mL/g for Pu were

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recommended for sensitivity analyses in the Addendum to the Work Plan (1998).

$K_d$ s also were determined for a crushed basalt. However, vesicles and fractures in basalt were assumed to be lined with minerals similar in sorption properties to those of the interbed sediment. Therefore, use of the interbed  $K_d$ s was suggested for modeling sorption of Am, Pu, and U in basalt. The basalt experiments and results are included in this review for the sake of completeness.

The following is an evaluation of the experimental procedures and results reported by Newman and others (1995). Some of the experiments were conducted at Clemson University (Goff, 1994). Other experiments were conducted by INEEL personnel.

### 5.3.1 Materials and methods

A combination of batch and column experiments were used to determine  $K_d$ s for Am, Pu, and U in basalt and interbed sediment.

#### 5.3.1.1 Solid phases

##### 5.3.1.1.1 Interbed sediments

Five interbed samples from various depths were composited, and the <0.25-mm size fraction was used for the experiments. This fraction was a sandy loam (table 5-3). Major minerals in the sand-sized fraction were pyroxene, plagioclase, quartz, olivine, and magnetite. The clay-sized fraction consisted of mica, montmorillonite, vermiculite, and chlorite. Some Mn and Fe oxide coatings were present. Cation exchange capacity was 17.39 meq/100 g.

##### 5.3.1.1.2 Basalt

A boulder from near the SDA was used to determine  $K_d$ s for Am, Pu, and U in the INEEL basalt. Cores were drilled from the boulder for use in intact basalt column experiments. The remainder of the boulder was crushed for use in crushed-basalt batch and column experiments. Only the <2-mm size fraction was used. This fraction was mostly coarse sand and some silt (table 5-3). Major minerals were pyroxene, plagioclase, and olivine. The cation exchange capacity was 6.04 meq/100 g.

#### 5.3.1.2 Aqueous phase

Synthetic ground water was used in the batch and column experiments. The water was formulated on the basis of analyses from the SRP aquifer (Wood and Low, 1986). The synthetic ground water used by Newman and others (1995) contained smaller concentrations of most constitu-

ents than did the average ground water reported by Wood and Low (1986) and smaller concentrations than have been measured in the perched water beneath the SDA (table 5-4). Actinides were added to the synthetic ground water from stock solutions. The initial chemical form of these stock solutions was: U as uranium nitrate in the VI oxidation state, Am as americium chloride in the III oxidation state, and Pu as plutonium nitrate in the IV oxidation state. Upon addition of the Pu stock solution to the synthetic ground water, the oxidation state changed. About 5 percent was Pu(III), 40 percent was Pu(IV), 50 percent was Pu(V), and 5 percent was Pu(VI). About half of the Pu(IV) was in the form of colloids greater than 0.1  $\mu$ m in size.

#### 5.3.1.3 Column experiments

##### 5.3.1.3.1 Crushed basalt and interbed sediments—saturated

Standard procedures were used for packing the columns and conducting the leaching experiments. The crushed-basalt and interbed columns were polyvinylchloride, 15.1 cm long and 2.5 cm inside diameter. This is an adequate length:width ratio for establishing one-dimensional advective-dispersive flow.

Synthetic ground water without actinides was eluted through the columns until pH and conductivity of column effluent were the same as those of the influent. About one pore volume of synthetic ground water containing Am, U, or Pu, then was added to each column, and leached with 200 pore volumes of actinide-free ground water.  $^3\text{H}$  also was added as a conservative tracer. Replicate columns were used for Am and U; three to five columns were used for Pu. Average pore-water velocities were 6 m/d. Velocities as slow as 0.6 m/d and as fast as 60 m/d were evaluated. Columns were saturated and leached from bottom to top.

Synthetic ground water containing Br and  $^{90}\text{Sr}$  also was eluted through two columns packed with crushed basalt. These experiments were designed to identify any differences between transport under saturated- and unsaturated-flow conditions.

##### 5.3.1.3.2 Intact basalt—saturated

The intact basalt cores (20.3 by 3.8 cm) were sealed in polymeric resin, then placed in polycarbonate tubes and the annular space filled with resin. They were filled and leached in the same manner as those containing unconsolidated cores. The intact basalt column experiments eluted contaminated ground water until the effluent concentrations were equal to the influent concentrations. Only  $^{90}\text{Sr}$  and the conservative tracer Br were used.

Table 5-2. Summary of K<sub>d</sub>s obtained using batch and column tests reported by Dicke (1997) (modified from Newman and others, 1995)

[mL/g, milliliters per gram; EDTA, ethylenediaminetetraacetic acid]

Isotope	Media	Batch test K <sub>d</sub> (mL/g)	Column test K <sub>d</sub> (mL/g)	Enhanced mobility K <sub>d</sub> (mL/g)	Recommended for risk assessment K <sub>d</sub> (mL/g)
<sup>241</sup> Am	Basalt	70-280		0.18	450**
<sup>241</sup> Am	Interbed	450-1,100		*	450
<sup>239</sup> Pu (total)	Basalt			0.25	5,100**
<sup>239</sup> Pu (total)	Interbed			*	5,100
Pu(V)	Basalt	70-130			
Pu(V)	Interbed	5,100-7,900			
Pu(V)	Surface Soil	7,800-22,000			
Pu(VI)	Basalt	12-24			
Pu(VI)	Interbed	110-690			
Pu(VI)	Surface Soil	1,800-4,900			
Pu(EDTA)	Basalt	0.04-0.05			
Pu(EDTA)	Interbed	4-5			
Pu(EDTA)	Surface Soil	40-490			
<sup>233</sup> U	Basalt	4-6	0.2-0.3		3**
<sup>233</sup> U	Interbed	3-6	9		6

\*Although enhanced mobility fraction was observed, it was too small to be modeled.

\*\*The assumption was made that sorption in basalt was controlled by minerals lining the fractures and having the same sorption capacity as that of the interbed sediment.

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Table 5-3. Particle-size distribution for five interbed sediments and their composite, and for crushed basalt used in  $K_d$  experiments at the Idaho National Engineering and Environmental Laboratory (modified from Goff, 1994)

Size (mm)	Interbed-1 (percent)	Interbed-2 (percent)	Interbed-3 (percent)	Interbed-4 (percent)	Interbed-5 (percent)	Composite interbed (percent)	Crushed basalt (percent)
>2	12.7	33.8	Not reported	38.6	9.4	16.7	Not reported
1.0-2.0	13.9	16.8	1.6	17.3	1.9	12.2	50.6
0.5-1.0	12.9	12.4	3.1	9.8	1.8	12.2	26.7
.25-.5	29.4	14.7	3.6	10.9	2.5	15.5	6.3
.1-.25	27.6	26.9	3.9	9.4	10.2	20.9	3.9
.05-.1	6.5	13.3	10	27.6	25.3	12.9	0.9
.002-.05	7.8	13.6	59.5	22.2	53.4	22.4	8.5
<.002	2	2.3	18.3	2.7	4.9	3.9	3.1

Table 5-4. Composition of synthetic ground water, water from the Snake River Plain aquifer, and perched and soil-zone water (from Newman and others, 1995)

[mg/L, milligrams per liter]

Constituent	Synthetic ground water*	Snake River Plain aquifer**			Perched and soil zone water***		
	Base chemistry (mg/L)	Average (mg/L)	Maximum (mg/L)	Minimum mg/L)	Average (mg/L)	Maximum (mg/L)	Minimum (mg/L)
Ca	11.5	51	120	5.0	41	70	26
K	9.8	4	12	0	5.8	12	1.0
Mg	8.3	18	54	0.2	17	25	14
Na	19.7	26	140	4.0	53	120	7
Cl	18.9	28	230	1.8	41	81	14
SO <sub>4</sub>	23.4	41	218	1.8	45	120	10
HCO <sub>3</sub>	96.6	220	510	52	190	280	120
F	0.5	0.6	11	0.03	0.3	0.6	0.2
SiO <sub>2</sub>	10.0	50	138	5.8	21	34	13
pH	8.0	7.8	9.1	7.0	8.2	9.1	7.7
I(mol/l)	0.0048	0.008	0.02	0.004			

\*Newman and others, 1995; \*\*Wood and Low, 1986; \*\*\*Rightmire and Lewis, 1987b (table 4-4, this report)

#### 5.3.1.3.3 Crushed basalt—unsaturated

Unsaturated column experiments were conducted to compare  $K_d$ s from saturated and unsaturated columns. Crushed basalt was used. Columns were 25.4 cm long and 2.77 cm inside diameter. The same column was used for six unsaturated experiments and one saturated experiment. Moisture content of the columns ranged from 29 to 49 percent of saturation. Br and  $^{90}\text{Sr}$  were added as tracers.

#### 5.3.1.4 Batch experiments

The batch test design was adapted from the American Society for Testing Materials (ASTM) method D4319 (1993). Solid:liquid ratios were chosen to remove enough reactant so that a change in concentration could be measured. For interbed experiments conducted by Goff (1994), solid concentrations ranged from 3.5 to 150 g/L, and basalt concentrations ranged from 20 to 500 g/L. For the INEEL crushed-basalt experiments, solid concentrations ranged from 100 to 700 g/L. The aqueous and solid phases were separated by filtering through a 0.2  $\mu\text{m}$  cellulose acetate filter or by centrifuging at 3,200 rpm for 20 minutes. Goff (1994) used 15-mL polystyrene centrifuge tubes. Duplicates with appropriate blanks were equilibrated for 14 time periods ranging from 5 minutes to 400 hours. INEEL personnel used 50-mL polycarbonate centrifuge tubes for Am and Pu. Before the actinides were added, basalt and sediments were prerinsed with uncontaminated ground water for two 12 hour periods.

### 5.3.2 Results and discussion

#### 5.3.2.1 Batch experiments

The  $K_d$ s used in the IRA model were determined from the batch experiment results which are presented first. Results from the column experiments and other assorted experiments then follow. The following results are from batch experiments conducted at Clemson University.

$K_d$ s for the batch experiments were calculated for 400 hours of equilibration. Equilibrium concentrations of U in the crushed basalt were attained within 61 hours, and in the interbed sediment, within 103 hours. Time required to attain equilibrium for Am and Pu was not given.

##### 5.3.2.1.1 Am

The INEEL  $K_d$ s for  $^{241}\text{Am}$  in interbed sediments reported by Dicke (1997) ranged from 450 to 1,100 mL/g (table 5-2). These values were obtained using initial

concentrations ranging from 3.5 to 15 Bq/mL (28 to 119  $\mu\text{g/L}$ ). The initial sediment concentration was 2.5 g/L. Individual  $K_d$ s for each concentration were not reported; however, it is apparent that the  $K_d$ s for Am were dependent on initial concentration. This is indicative of nonlinear sorption, where the relative amount sorbed decreases as aqueous concentration increases. Thus the largest  $K_d$  of 1,100 mL/g would represent the smallest initial concentration of 3.5 Bq/mL, and the lowest  $K_d$  of 450 mL/g represents the initial concentration of 15 Bq/mL. For Am concentrations outside the range used in these experiments,  $K_d$ s could be either larger or smaller.

Sorption of Am by the crushed basalt was also apparently nonlinear. Distribution coefficients ranged from 70 to 280 mL/g. Initial Am concentrations ranged from 1.38 to 7.34 Bq/mL (11 to 58  $\mu\text{g/L}$ ), and the initial sediment concentration was 12.5 g/L.

##### 5.3.2.1.2 U

Only one initial concentration and one solid concentration were used to determine U  $K_d$ s. For the interbed sediment, a  $K_d$  of 5.1 mL/g (table 5-2) was calculated using an initial concentration of 69.05 Bq/mL and a solid concentration of 6.8 g/L. A  $K_d$  of 4.7 mL/g for the crushed basalt was calculated using an initial concentration of 5.94 Bq/mL, and a solid concentration of 200 g/L.

##### 5.3.2.1.3 Pu

The mobility of Pu is affected by its oxidation state, which can be III, IV, V, or VI. More than one oxidation state can coexist in solution. The III and IV oxidation states predominate under reducing conditions, and the V and VI oxidation states predominate under oxidizing conditions. As was previously mentioned, the oxidation state of Pu after it had been added to the synthetic ground water was a mixture of all four, although the IV and V states dominated. To evaluate changes in oxidation state with time, a 14-day experiment was conducted in which synthetic ground water spiked with Pu(IV) was allowed to equilibrate. The amount of Pu(III, V, VI) remained relatively constant; however, within the first 24 hours, Pu(IV) activity in the solution phase decreased by 50 percent. This decrease in activity was attributed to settling of polymerized Pu(IV). Between 1 and 14 days, the Pu distribution remained relatively constant. After 14 days, the container was shaken and Pu activity increased to 90 percent of the initial value because of resuspension of most of the polymerized Pu(IV). From this experiment, it was concluded that Pu(IV) is essentially insoluble and that a  $K_d$  for this oxidation state would be inappropriate. Therefore,

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only the Pu(V) and Pu(VI) oxidation states were used in batch experiments to determine  $K_d$ s.

Pu(V)  $K_d$ s for the interbed sediment ranged from 5,100 to 7,900 mL/g (table 5-2). Pu(V)  $K_d$ s for a surface soil included in these experiments ranged from 7,800 to 22,000 mL/g. The smallest value of 5,100 mL/g was used in the IRA modeling. Pu(VI)  $K_d$ s were smaller, ranging from 110 to 690 mL/g for the interbed sediment, and from 1,800 to 4,900 mL/g for the surface soil. Sorption of Pu in the presence of EDTA was significantly less. In the presence of EDTA,  $K_d$ s for the interbed sediment averaged about 5 mL/g, and for the surface soil, about 400 mL/g. In these experiments, the initial Pu concentration remained constant, but the solid concentration was varied. Therefore, nonlinear sorption of Pu could not be evaluated. Sorption tended to increase with solids concentration, but the trend was not consistent. In addition, at small suspended solids concentrations, Pu remained in the initial oxidation state (either V or VI). However, at larger suspended solids concentrations, Pu(V) reduced to Pu(IV) and Pu(VI) to Pu(V). This reduction was attributed to mediation by Fe and/or Mn containing minerals.

Pu(V)  $K_d$ s for crushed basalt ranged from 70 to 130 mL/g. Pu(VI)  $K_d$ s were much smaller, ranging from 12 to 24 mL/g. Sorption of a Pu(EDTA) complex was minimal;  $K_d$ s averaged about 0.4 mL/g.

### 5.3.2.2 Risk assessment $K_d$ s for Am, U, and Pu

$K_d$ s for crushed basalt were not used in the IRA model. This decision was justified for several reasons. Crushed basalt has a high percentage of fresh mineral surfaces not present in the aquifer. These surfaces will have sorption properties that are different from those of minerals lining basalt fractures and vesicles. Also, the surface area of crushed basalt most likely will not be comparable to that of basalts in the aquifer. In addition, Barney (1981) showed that freshly crushed basalt of the Columbia River group slowly weathers during the course of laboratory experiments.  $K_d$ s measured under such conditions risk being affected by changing sorption properties.

The proposed  $K_d$ s for Am, U, and Pu in the interbed sediments should be used with caution for IRA modeling. Each  $K_d$  represents one unique measuring point in a complex geochemical environment. Combining the five interbed samples homogenized sediments that have different grain-size distributions and mineralogy. Each of these individual sediments could have different sorption properties. In addition, using the <0.25-mm size fraction eliminated 40 percent of the solids and biased the  $K_d$  toward larger values because of the greater surface area of the finer-size fraction used in the experiments.

The assumption that fractures and vesicles in the basalt have the same sorption properties as the interbed sediments may or may not be accurate. Minerals present in basalt fractures tend to be finer grained, such as clay minerals, or in the form of precipitates, such as calcite. Although these types of minerals are also present in the interbed sediments, their sorption properties may be different from those of the bulk interbed material, which also contains coarser particles of different mineralogy (sand-size grains of quartz and feldspar).

The synthetic ground water used by Newman and others (1995) contained smaller concentrations of most constituents than did the average ground water reported by Wood and Low (1986) and smaller concentrations than did perched and soil-zone water (table 5-4). Sorption of Am, U, and Pu is affected by aqueous speciation. All three actinides form aqueous  $\text{CO}_3$  complexes. In general, sorption decreases as  $\text{CO}_3$  concentrations increase. Thus, the  $K_d$ s determined for the synthetic ground water may be different from  $K_d$ s for perched ground water.

### 5.3.2.3 Column experiments

The following results are for column experiments conducted at Clemson University.

#### 5.3.2.3.1 Interbed sediment columns

Tritium was used as a conservative tracer to evaluate column packing. Breakthrough curves for  $^3\text{H}$  matched the shape expected for one dimensional advective-dispersive transport of a nonreactive solute (fig. 5-5). Channeling was not observed in any of the columns.

Essentially all of the Am was removed from two columns containing interbed sediment; however, there was still a small enhanced-mobility spike within the first five pore volumes (fig. 5-6). About 1.8 percent and 1.9 percent of the Am applied initially was recovered after elution of 200 pore volumes of actinide-free ground water. Most of the Am remaining in the columns was distributed in the first 3 cm.

Most of the Pu applied in the initial spike also was removed from three interbed sediment columns. There was still a small enhanced-mobility spike within the first five pore volumes (fig. 5-7). About 0.01 percent, 0.1 percent, and 0.15 percent of the applied Pu was recovered. No measurements of the distribution of the remaining Pu were reported.

About 90 and 99 percent of the applied U was recovered from two columns; however, the breakthrough curves were delayed by about 20 to 30 pore volumes (fig. 5-8).  $K_d$ s calculated from the retardation factors were 12 and 9 mL/g for the two columns studied.

One potential problem with the interbed column experiments is the increase in initial influent pH of 8 to about 8.4. Conductivity also increased. These observations, plus the fact that the influent feed solution was undersaturated with respect to calcite, indicate calcite dissolution during the column experiments. Geochemical calculations indicate that a 0.4-unit change in pH can change the  $K_d$  for U by a factor of 3 or 4. Calcite dissolution also may have an effect on Am and Pu transport in these experiments.

#### 5.3.2.3.2 Crushed-basalt columns

Tritium was used as a conservative tracer to evaluate column packing. Breakthrough curves for  $^3\text{H}$  matched the shape expected for one-dimensional advective-dispersive transport of a nonreactive solute (fig. 5-9). Channeling was not observed in any of the columns.

After elution of 200 pore volumes of actinide-free ground water, the amount of Am recovered in effluent from two columns containing crushed basalt was 9 and 14 percent of the total concentration added initially. Most of the Am eluted between pore volumes 1 and 3, in what is referred to as an enhanced-mobility fraction (fig. 5-10). The maximum Am concentration in this fraction was about 20 percent of the influent concentration. After this initial spike, effluent concentrations became constant between 0.01 and 0.1 percent of influent concentration. Analytical detection limits were not reported. Retardation factors for the enhanced-mobility fraction in the two columns were 1.6 and 1.7, equivalent to a  $K_d$  of 0.18 mL/g (table 5-2). Gamma scans revealed that the Am remaining was distributed throughout the length of the columns.

After eluting with 200 pore volumes of actinide-free ground water, the amount of Pu recovered in effluent from five columns containing crushed basalt was 10 percent, 17 percent, 24 percent, 34 percent, and 57 percent, of the total initial concentration added. Some of the Pu eluted in an enhanced-mobility fraction between pore volumes 1 and 3, similar to the elution of Am. After the initial Pu spike, concentrations slowly decreased over 200 pore volumes (fig. 5-11). Maximum Pu concentrations in the initial spike ranged from 20 to 50 percent of the influent concentration. Retardation factors for the enhanced-mobility fractions were about 2, equivalent to a  $K_d$  of 0.25 mL/g (table 5-2). The distribution of Pu remaining in the columns was not determined.

After eluting with 200 pore volumes of actinide-free ground water, essentially all (94 and 104 percent of the total initial concentration) of the U was recovered from two columns containing crushed basalt. U concentrations in column effluent began to increase at about pore volume

1 and peaked at pore volume 2. Concentrations then slowly decreased throughout the remainder of the experiments (fig. 5-12). Retardation factors were 1.6 and 2, equivalent to  $K_d$ s of 0.2 and 0.3 mL/g (table 5-2). Maximum concentrations were 60 to 70 percent of the influent concentration. Early elution of U was assumed to be related to weak sorption of the aqueous phase as opposed to the presence of an enhanced-mobility fraction.

#### 5.3.2.3.3 Enhanced mobility fraction

The enhanced-mobility fraction responsible for the early elution of Am and Pu (figs. 5-6, 5-7, 5-10, and 5-11) indicates that both actinides may move in the subsurface at a significantly faster rate than predicted by equilibrium-based distribution coefficients. At least three possible mechanisms could explain the enhanced mobility of Am and Pu: (1) transport as a colloid, (2) transport as a weakly sorbing aqueous complex, and (3) slow reaction kinetics.

Other researchers have found Am to be associated with colloidal material (Means and others, 1978a; Travis and Nuttall, 1985; Penrose and others, 1990; Moulin and others, 1991). Both Pu (Choppin and Stout, 1989) and Am (Nash and others, 1988) have been shown to strongly sorb on silica. It is possible that Am and Pu sorbed on fine-grained material created during the basalt crushing process. These grains then could have been removed during leaching. Colloids also could have formed in the columns by *in situ* weathering reactions of the fresh basalt. Barney (1981) observed evidence for weathering in experiments with freshly crushed basalts from the Columbia River group.

Hydrolysis products of Am and Pu could have formed colloids. It is clear from the shape of the breakthrough curves that Pu was more mobile than Am. The Pu-oxidation-state experiment showed that colloidal Pu(IV) can form in synthetic ground water. This experiment indicated that Pu(IV) and (V) were the dominant oxidation states of the initial solution. Most Pu(IV) was likely present as a colloid, and some could have been transported through the columns. The Pu(V) could have been sorbed to the stationary phase or sorbed and transported as a colloid.

The enhanced-mobility fraction also could represent transport as a mobile aqueous  $\text{CO}_3$  complex. In a separate experiment with Pu, increasing alkalinity from 0.05 to 1.1 g/L as  $\text{CaCO}_3$  increased the apparent enhanced-mobility fraction from 52.2 to 78 percent.

Kinetically-limited sorption could account for the enhanced-mobility fraction. In column tests with Am, increasing the flow rate from 0.6 to 60 m/d increased the enhanced-mobility fraction of Am from 1.3 to 43 percent,

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although the location of the peaks did not change. The faster flow rates may have increased the mass of mobile colloids or decreased contact time between actinide and sorbing material.

### 5.3.2.4 Additional experiments

Several other experiments were conducted to investigate various aspects of sorption in this system. These are briefly summarized in the following sections.

#### 5.3.2.4.1 pH and ionic-strength variability

Effects of pH and ionic strength on sorption were evaluated for U in a series of batch experiments. Synthetic ground water spiked with U was used as a base solution. Ionic strength was increased from 0.004 to 0.01 and 0.02 by addition of K or  $\text{CaCl}_2$ . pH was adjusted to 6, 8, or 10. For crushed basalt, U sorption decreased with increasing Ca concentration and increasing pH. K had little effect on U sorption. At lower pH values,  $\text{UO}_2^{2+}$  and  $\text{Ca}^{2+}$  likely compete for sorption sites. As pH increases, U complexation with  $\text{CO}_3$  results in less sorption. Trends were similar for interbed sediment but differences were not as great. No  $K_d$ s were reported; however, these data point out the dependency of sorption on ground-water composition.

#### 5.3.2.4.2 Reproducibility of $K_d$ s

Batch experiments were used to compare  $K_d$ s for  $^{90}\text{Sr}$  sorption in experiments conducted at Clemson University and the INEEL.  $K_d$ s were comparable; however, initial differences in aqueous concentration and solids concentration did not allow a statistical evaluation. No data were provided on the reliability of Am, Pu, and U  $K_d$ s.

#### 5.3.2.4.3 Solid:liquid ratio

$K_d$ s measured in batch tests can decrease as suspended solids concentration increases. Possible explanations include (1) an increase in proximity of solids resulting in decreased surface area available for sorption, (2) an increase in the amount of stagnant water in grain fractures and pore spaces, resulting in more time needed for diffusion to sorption sites, and (3) an increase in the proportion of colloidal material that may not be removed by filtration, resulting in apparent greater aqueous concentrations.

$^{90}\text{Sr}$   $K_d$ s decreased from 2.8 mL/g at a solid:liquid ratio of 0.1, to 1.9 mL/g at a solid:liquid ratio of 1.9. There apparently was some effect of solid:liquid ratio on sorption, but only when solid:liquid ratios exceeded 0.7. These data do not necessarily apply to the actinides. For Pu(V) and Pu(VI) sorption by the surface soil,  $K_d$ s did decrease

as solids concentration increased; however, the data were inconclusive for the interbed sediment and crushed basalt.

#### 5.3.2.4.4 Crushed basalt versus intact basalt

Experiments using crushed versus intact basalt were conducted only with Br and  $^{90}\text{Sr}$ ; however, some basic observations may be generic enough to extrapolate to Am, U, and Pu. Unfortunately, different scales were used to plot the data, so it is difficult to make direct comparisons.

Breakthrough curves for  $^{90}\text{Sr}$  in crushed basalt columns were typical of those for advective-dispersive flow.  $^{90}\text{Sr}$   $K_d$ s were about 3.5 mL/g. Breakthrough curves for  $^{90}\text{Sr}$  in intact basalt cores did not resemble those expected for advective-dispersive flow in one dimension. A breakthrough of about 60 percent of the initial concentration was followed by a very slow increase in concentration. Two retardation factors of about 1 were calculated, equivalent to a  $K_d$  of 0.3 mL/g. This value is significantly smaller than the  $K_d$ s for  $^{90}\text{Sr}$  in the crushed basalt and interbed sediment. The larger  $^{90}\text{Sr}$   $K_d$ s indicate that transport of  $^{90}\text{Sr}$  through the fractures in the intact basalt was too rapid for equilibrium sorption, or that the sorption properties of the basalt fractures were different from the sorption properties of the crushed basalt and interbed sediment.

In summary, contaminant transport in intact basalt cores did not follow traditional patterns of advective-dispersive flow models. Transport may be dominated by preferential flowpaths and diffusion into and out of the basalt matrix. When flow through fractured media is anticipated, the sorption rate constant should be compared with the hydraulic residence time to evaluate whether equilibrium conditions exist.

#### 5.3.2.4.5 Unsaturated column experiments

Crushed-basalt columns were used for unsaturated column experiments. Water content ranged from 33 to 50 percent of saturation. Both Br and  $^{90}\text{Sr}$  breakthrough curves and  $K_d$ s were similar to those in the saturated crushed basalt experiments. Newman and others (1995) concluded that saturated-column  $K_d$ s can be applied to sorption in the unsaturated zone.

### 5.3.3 Summary of the evaluation of $K_d$ s for Am, U, Np, and Pu used in the Interim Risk Assessment

$K_d$ s determined in these experiments for Am, U, and Pu are listed in table 5-2. Also listed are the  $K_d$ s recommended for use in the IRA model. Specific concerns



regarding the K<sub>d</sub>s recommended for use in the IRA model are presented here.

(1) The concentrations of major cations and anions in the synthetic ground water used in these experiments are generally smaller than the concentrations measured in perched and infiltrating water at the SDA. This could result in underestimating the amount of aqueous complexation of Am, U, and Pu, and overpredicting sorption. Thus, the recommended K<sub>d</sub>s could be too large. Larger concentrations of cations and anions also could increase competition for sorption sites, thereby decreasing actinide sorption. If there was calcite dissolution, as indicated by the column experiments, then the final solution composition could have been closer to that of natural waters; however, final compositions apparently were not determined.

(2) Sorption of Am as a function of aqueous concentration was apparently nonlinear. Sorption of Pu and U was probably nonlinear as well. This means that the measured K<sub>d</sub>s are relevant only for the concentrations used in the experiments. Concentrations at the SDA that are outside of the range used in these experiments will have K<sub>d</sub>s that are either smaller or larger than those reported here.

(3) The experimental data show that Pu sorption is highly dependent on oxidation state. The K<sub>d</sub> recommended for IRA modeling is for Pu(V) and would not be applicable to the more mobile Pu(VI).

(4) The K<sub>d</sub>s recommended in the IRA model are from the fine-grained fraction of one composite interbed sample that has not been shown to represent the range of sorption properties in the unsaturated zone.

(5) The assumption that sorption properties of the interbed sediments are comparable to those of the fractures in the basalts needs to be verified.

(6) The enhanced-mobility fraction responsible for the early elution of Am and Pu in the column experiments raises questions about the mechanisms responsible for transport of Am, U, and Pu. If this fraction represents transport as aqueous complexes, then the K<sub>d</sub>s used in the IRA model are too large. If the actinides are transported as colloids, basing risk assessment on sorption-controlled transport may need to be reevaluated.

(7) In these experiments, any actinide passing through a 0.2-μm membrane filter or removed from solu-

tion by centrifugation for 20 minutes at 3,200 rpm was considered dissolved. Other researchers have shown that neither of these procedures necessarily removes all colloids from solution. If some of the Am, U, or Pu assumed to be dissolved were present as colloids, the apparent aqueous-phase concentration would be larger, resulting in smaller calculated K<sub>d</sub>s. From a solute transport perspective, underestimating K<sub>d</sub>s would result in an increase in the predicted transport distance of an actinide.

## 5.4 Evaluation of the K<sub>d</sub>s for Np used in the Interim Risk Assessment model—literature review

The K<sub>d</sub> for Np used in the IRA model was 8 mL/g, based on a range of 1 to 80 mL/g. These values are from Dicke (1997) and were selected from the literature. In the Addendum to the Work Plan, a sensitivity analysis for Np was proposed using Np K<sub>d</sub>s of 4 mL/g (half the base case) and 16 mL/g (twice the base case). For basalt, the assumption was made that fracture surfaces were lined either with fine-grained sediments or with chemical alteration products that resulted from water movement along the fractures over extended periods of time (Becker and others, 1998). Therefore, the same K<sub>d</sub>s used to simulate sorption on sediments were used to simulate transport through basalt.

Dicke (1997) selected Np K<sub>d</sub>s from three sources, each a compendium of K<sub>d</sub>s from the literature (Baes and Sharp, 1983; Ticknor and Ruegger, 1989; Sheppard and Thibault, 1990). All the references in these three compendiums have been evaluated for their applicability to the INEEL. The review presented in this report is not an exhaustive review of Np sorption, but a review of those references upon which the K<sub>d</sub>s cited by Dicke (1997) are based. The approach used in this review was to summarize the experiments and results in two different tables. Data from those references that are possibly relevant to the INEEL are summarized in table 5-5 and discussed in detail in this report. Those references not considered to be relevant to the INEEL are summarized in table 5-6. Unless specified otherwise, all experiments refer to the Np(V) oxidation state.

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Table 5-5. Np  $K_d$ s from references considered applicable to the Idaho National Engineering and Environmental Laboratory

[ $K_d$ s, distribution coefficients; mL/g, milliliters per gram]

Reference	Solid phase	Location of sample	$K_d$ s (mL/g)
Barney (1981)	Altered basalt	Hanford	17-70
Barney (1981)	Secondary minerals from basalt	Hanford	13-100
Barney (1982)	Sandstone	Hanford	13-20
Barney (1982)	Tuff	Hanford	17-33
Salter and others (1981b)	Secondary minerals	Hanford	40
Routson and others (1977)	Washington soils	Washington	2.4-3.9
Sheppard and others (1979)	Idaho soils	Idaho	38-142
Dicke (1997)	Literature review	Variable	1-80

Table 5-6. Np  $K_d$  references not considered applicable to the Idaho National Engineering and Environmental Laboratory

[ $K_d$ s, distribution coefficients]

Reference	Summary of experiments	Reasons for rejecting $K_d$ s	Additional comments
Dahlman and others (1976)	Batch Np sorption experiments on clay	Experimental conditions not applicable to those at the INEEL	
Nishita and others (1979)	Batch Np sorption experiments using seven soils	Inadequate data on soil properties and aqueous chemistry for comparison with the INEEL data	Np sorption increased with pH
Allard and others (1980)	Batch Np sorption experiments using freshly crushed individual minerals and granite	Use of individual mineral phases inappropriate for comparison with the INEEL data. Crushing not appropriate	Np sorption increased between pH 7 and 9
Ames and Rai (1978)	Review of Np sorption literature	$K_d$ s cited here described in other references	
Johnston and Gillham (1980)	Review of Np sorption literature	$K_d$ s cited here described in other references	
Coughtrey and others (1985)	Review of Np sorption literature	$K_d$ s cited here described in other references	
Nishita and others (1981)	Soils contaminated with Np, then extracted with acetate, Ca and pure water	No estimates of $K_d$ s. Not enough data to calculate $K_d$ s	

Table 5-6. Np K<sub>d</sub> references not considered applicable to the Idaho National Engineering and Environmental Laboratory—Continued

Reference	Summary of experiments	Reasons for rejecting K <sub>d</sub> s	Additional comments
Seitz and others (1979)	Np eluted through sandstone columns	No K <sub>d</sub> data given	A small fraction of Np eluted with nonreactive tracer, indicating possible colloid transport or channeling of aqueous Np
Seitz and others (1978)	Batch Np sorption experiments using various rock types and distilled water	Solid and aqueous phases not applicable to the INEEL	
Anderson and others (1982)	Batch Np sorption experiments using several rock types and pure mineral phases	Solid phases not applicable to the INEEL data. Crushing inappropriate	
Barney (1984)	Batch Np sorption experiments using basalts and interbed materials from Hanford, Wash.	Experimental data fitted to Freundlich isotherm. No K <sub>d</sub> data given.	
Bondietti and Francis (1979)	Batch Np sorption experiments using crushed igneous rocks and shales under reducing conditions	No K <sub>d</sub> data given	Increased sorption of Np with time interpreted as kinetically controlled reduction of NpO <sub>2</sub> <sup>+</sup> to NpO <sub>2</sub> and increased sorption
Meyer and others (1983)	Recirculating column experiment with alumina	Insufficient information on aqueous phase. Solid phase not applicable to the INEEL	Np sorption increased with pH
Nakayama and others (1988)	Np leached through quartz-packed column.	Experimental conditions not applicable to those at the INEEL	Some Np eluted with nonreactive tracer, indicating colloidal transport
Salter and others (1981b)	Batch Np sorption experiments with crushed basalts	Crushed basalts not representative of Np sorption in basalt fractures at the INEEL	
Sheppard and others (1987)	Np eluted through soil cores from Canada	Aqueous- and solid-phase chemistries different from those at the INEEL	
Thibault and others (1990)	Review of Np sorption literature	K <sub>d</sub> s cited here described in other references	

### 5.4.1 Studies of potential relevance to the Idaho National Engineering and Environmental Laboratory

Routson and others (1977) conducted batch sorption experiments for  $^{237}\text{Np}$  on subsoil samples from Washington and South Carolina. The Washington soil had a pH of 7, 0.8 mg/g  $\text{CaCO}_3$ , a cation exchange capacity (CEC) of 4.9 meq/100 g, 10 percent silt, and 0.5 percent clay. The South Carolina soil had a pH of 5.1, <0.2 mg/g  $\text{CaCO}_3$ , a CEC of 2.5 meq/100 g, 3.6 percent silt, and 37 percent clay. Sorption was measured in solutions with variable concentrations of  $\text{Ca}(\text{NO}_3)_2$  or  $\text{NaNO}_3$ . The initial Np concentration was 3.7  $\mu\text{Ci/L}$  for the Washington soil and 1  $\mu\text{Ci/L}$  for the South Carolina soil. The solution:solid ratio was 25 mL/10 g. Equilibration was for 24 hours, followed by centrifugation at 4,000 rpm for 3 minutes. Selected samples also were filtered through 0.01- and 0.45- $\mu\text{m}$  filters; there was no difference in Np concentration.

Np  $K_d$ s decreased with increasing concentrations of Ca and Na. For the Washington soil,  $K_d$ s ranged from 0.36 mL/g in 0.2 mol Ca, to 2.4 mL/g in 0.002 mol Ca, and from 3.1 mL/g in 0.3 mol Na to 3.9 mL/g in 0.015 mol Na. For the South Carolina soil,  $K_d$ s ranged from 0.16 mL/g in 0.2 mol Ca to 0.25 mL/g in 0.002 mol Ca and from 0.43 mL/g in 0.2 mol Na to 0.66 mL/g in 0.002 mol Na.

$K_d$ s for the stronger ionic solutions are probably unrealistic for the INEEL. In addition, water at the INEEL has a more complex chemistry than water with only Ca, Na, and  $\text{NO}_3$ . The pH of the South Carolina soil (5.1) is much lower than that of the INEEL soils (about 8). Composition of the Washington soil appears to be similar enough to that of the INEEL soils for consideration of the Np  $K_d$ s. Realistic  $K_d$ s from the Washington study that may have some transferability to the INEEL are 2.4 mL/g in 0.002 mol Ca at a pH of 7, and possibly 3.9 mL/g in 0.015 mol Na.

A report on Np sorption by Sheppard and others (1977) is referenced in Dicke's 1997 report; however, no details concerning the experiments are given in the Sheppard report. A later journal article describing the experimental details was published by Sheppard and others (1979) and is used in this review. Several soils were used in the experiments; four of the soils were from an unknown location at the INEEL. Quality control on radionuclide purity was good. Water:soil ratios were 10 mL/g. The initial Np concentration was 0.00025  $\mu\text{Ci/mL}$ , well below the concentration of any solubility products. Composition of the soils were a loam, two sandy-clay loams, and a loamy sand. Experimental data

on the effectiveness of centrifugation for particle separation show that the greater the centrifugation speed, the smaller the size of particle removed. For example, at 1,750 rpm, particles >65 nm are removed. At 7,000 rpm, particles >17 nm are removed.

Results are reported in terms of an effective distribution ratio,  $R^*$ , and were converted to  $K_d$ . For soil ID-A at pH 8.3, the  $K_d$  was 51.6 mL/g; for soil ID-B at pH 8.4, the  $K_d$  was 142 mL/g; for soil ID-C at pH 8.4, the  $K_d$  was 38 mL/g; and for soil ID-D at pH 7.7, the  $K_d$  was 38.7 mL/g. No obvious trend in  $K_d$  related to soil properties was apparent. Distilled water was used, and no final chemical composition was given. Because Idaho soils were used in these experiments, the  $K_d$ s are probably representative of soils at the INEEL but the experiments were limited by the use of only one Np concentration. Another limitation of the experiment was the use of low ionic-strength water which would cause overestimation of sorption.

A report by Barney (1981) describes experimentally determined  $K_d$ s for Np sorption on altered and unaltered basalt and on secondary minerals from Hanford. The unaltered basalt was glassy and came from the Columbia River group. The three major minerals were labradorite, augite, and magnetite. The basalt was crushed to a grain size of 20 to 50 mesh sieve number. The solid:liquid ratio was 1 g/30 mL, and pH values were 8.5 to 9.5. Suspensions were filtered through a 3-nm molecular filter. About 4 weeks were required for equilibrium, probably a result of the fresh basalt equilibrating with water. Sorption by the crushed, unaltered basalt was a function of concentration and Np oxidation state;  $K_d$ s ranged from 5.4 to 278 mL/g. Altered basalts contained about 40 percent vesicles and vugs filled with secondary minerals, either tuff or a clay-rich alteration.  $K_d$ s for altered basalts ranged from 27 to 8,688 mL/g. Secondary minerals scraped from altered basalts appeared to be primarily smectites;  $K_d$ s ranged from 23 to 219 mL/g.

The larger  $K_d$ s were the result of adding hydrazine to the experiments, which caused reduction of Np(V) to Np(IV).  $K_d$ s for Np(V) in unaltered basalt ranged from 2 to 20 mL/g, and averaged  $8.1 \pm 2.2$  mL/g with  $\text{NaHCO}_3$ , and  $7.5 \pm 0.4$  mL/g without  $\text{NaHCO}_3$ .  $K_d$ s for Np(V) in altered basalt ranged from 17 to 70 mL/g, and averaged  $44 \pm 20$  mL/g with  $\text{NaHCO}_3$ , and  $43 \pm 4$  mL/g without  $\text{NaHCO}_3$ .  $K_d$ s ranged for Np(V) in secondary minerals from 13 to 100 mL/g, and averaged  $32 \pm 8$  mL/g with  $\text{NaHCO}_3$ , and  $37 \pm 2$  mL/g without  $\text{NaHCO}_3$ . Because of the nonlinearity of sorption, Freundlich isotherms were fit to the data.

Barney's study (1981) is one of the more complete sorption studies experimentally. In addition, because the composition of basalt used in Barney's experiments was similar to that of the basalt at the INEEL, the secondary mineral assemblages probably are similar also. K<sub>d</sub>s for the secondary minerals were comparable to those of the crushed, altered basalts. All these values are within the 1 to 80 mL/g range considered by Dicke (1997).

Barney (1982) conducted later experiments similar to those described in his 1981 study, but isotherms were for a sandstone and a tuff interbed. In the presence of hydrazine, Np(V) was reduced to Np(IV) and strongly sorbed; K<sub>d</sub>s ranged from 1,000 to 5,000 mL/g. K<sub>d</sub>s for Np(V) ranged from 13 to 20 mL/g for sandstone and 17 to 33 mL/g for tuff. This data set complements that of the 1981 study.

Salter and others (1981a) conducted experiments using secondary minerals lining and filling vesicles, vugs, and fractures in basalt of the Columbia River group underlying Hanford; 98 percent of the secondary minerals were smectites, with minor FeOOH, calcite, and silica. Surface area was 546 m<sup>2</sup>/g, and CEC was 72 meq/100 g. For an initial Np concentration of  $7.47 \times 10^{-8}$  mol, the K<sub>d</sub> at 23°C was  $36.9 \pm 7.5$  mL/g and, at 63°C, was  $53.5 \pm 8.8$  mL/g. Water was a NaHCO<sub>3</sub> type with a pH of 8. The K<sub>d</sub> for a pH 10 Na-SiO<sub>2</sub> type water was 160 mL/g. This was a single concentration K<sub>d</sub>. Sediment and water used in this experiment may have been similar to those used in the INEEL experiments.

#### 5.4.2 Summary of K<sub>d</sub>s for Np used in the Interim Risk Assessment model

Experimental data from the literature cited in this section show that sorption of Np is a function of aqueous chemistry and solid-phase mineralogy. Most of the studies cited were for experiments conducted under oxidizing conditions, where Np(V) was the dominant oxidation state. The redox state in the unsaturated zone at the SDA is expected to be oxidizing. The two studies in which Np(V) was reduced to Np(IV) showed that much larger concentrations of Np were removed from solution, either by sorption or because of the lower solubility of Np(IV).

The dominant Np(V) species in solution in the absence of complexing ions is  $\text{NpO}_2^+$ . Sorption is a function of pH. Sorption of Np is minimal at low pH and increases with increasing pH. This behavior is characteristic of cations. Some of the experimental evidence has shown that increasing cation concentration, especially Ca, results in competition for sorption sites and less sorption of Np. Complexation of  $\text{NpO}_2^+$  with anions can result in

the formation of neutral or negatively charged species such as  $\text{NpO}_2\text{HCO}_3^0$  and  $\text{NpO}_2\text{CO}_3^-$ , which sorb weakly. Thus, as the concentration of these complexing ions increases, sorption of Np would be expected to decrease. Experimental data have shown that Np sorption is nonlinear. Measured K<sub>d</sub>s decrease as the initial concentration of Np increases. Sorption of Np also varied with solid-phase mineralogy. Freshly crushed samples of minerals and rocks tended to sorb less Np than did secondary mineral assemblages.

Measured K<sub>d</sub>s are dependent on the experimental conditions. For example, using different solid:solution ratios can result in different K<sub>d</sub> measurements. The method of aqueous phase separation is important. Very small colloids may not be removed by centrifugation or filtration through larger pore-size filters.

The experimental data show that there is a high degree of variability in Np sorption, depending on aqueous-phase chemistry and solid-phase mineralogy. This variability argues strongly for site-specific determination of Np K<sub>d</sub>s under geochemical conditions realistic for the INEEL. Experimental data from the Hanford studies (Barney, 1981, 1982; Salter and others, 1981a, 1981b) could be analogous to conditions at the INEEL, because basalt is the predominant rock type at both sites. The reported K<sub>d</sub>s are comparable to those chosen by Dicke (1997) (table 5-5). On the basis of all the data evaluated in the literature, a smaller K<sub>d</sub> of 8 mL/g for Np for use in the IRA model is not unreasonable. However, given the dependence of K<sub>d</sub> on aqueous chemistry and solid-phase mineralogy, the sorption behavior of Np should be determined for the range of geochemical conditions specific to the INEEL.

#### 5.5 Use and limitations of the K<sub>d</sub> concept as applied to actinide transport at the Idaho National Engineering and Environmental Laboratory

The K<sub>d</sub> concept has been introduced and discussed earlier in this report (section 5.2.1). The present section will compare the advantages and limitations of the K<sub>d</sub> approach with those of speciation-based approaches in simulating radionuclide transport. Wherever possible, reference will be made regarding the possible advantages and limitations in using either one of these approaches at the INEEL site.

##### 5.5.1 Advantages and limitations of the K<sub>d</sub> approach in

## modeling contaminant retardation

Sorption reactions are commonly a predominant cause of contaminant retardation in ground-water systems. The  $K_d$  approach in modeling such contaminant retardation has been widely implemented in computer codes that attempt to simulate the reactive transport of contaminants.

### 5.5.1.1 Advantages of the $K_d$ approach

The mathematical simplicity of the  $K_d$  approach is its primary advantage.  $K_d$ s are generally assumed constant over the transport domain and timescale considered and are easily incorporated into the advection-dispersion equation as part of a constant retardation factor,  $R$ , which modifies both the dispersive and the advective terms. Consequently, a computer code used to simulate the transport of conservative, nonreactive, components can be easily modified to solve the transport equation for a reactive "retarded" component.

In addition, experimental determinations of  $K_d$ s are relatively easy to perform.  $K_d$ s obtained from batch methods in the laboratory are particularly easy to obtain. Consequently, the number of  $K_d$  measurements has been described as "almost incalculable," as mentioned earlier in section 5.2.1. However, despite the prolific number of  $K_d$  measurements, the experimental conditions pertaining to the measurements are generally insufficiently controlled and are rarely adequately described.

### 5.5.1.2 Limitations of the $K_d$ approach

Despite its advantages of simplicity, the  $K_d$  approach has many limitations. Foremost,  $K_d$  measurement or estimation techniques, whether based on laboratory measurements or field observations, rarely consider all the chemical and physical processes that may be responsible for the partitioning of a constituent between mobile and immobile phases. The partitioning generally is considered to involve a reversible sorption process, even though the constituent of interest also may have undergone partitioning due to (1) chemical processes such as solid-phase precipitation; formation of, or partitioning into, a solid-solution phase; volatilization, or (2) physical processes such as diffusion into immobile-fluid zones. Generally, comparison of the transport of a reactive tracer with that of a conservative tracer may permit accounting for retardation caused by physical processes.

Despite the assumption that  $K_d$ s generally account for partitioning caused by sorption of a constituent onto mineral surfaces,  $K_d$ s are normalized to a given mass of solid material instead of being normalized to a given solid

surface area. The effect of surface-to-mass ratios, or grain size, on  $K_d$  determinations and the effects that rock crushing may have on  $K_d$  determinations are often not accounted for. The sorptive properties of a freshly fractured rock surface, full of crystal dislocations created by the crushing process, and without the presence of any secondary minerals generated by natural weathering of the primary mineral, can be expected to differ significantly from those of an ancient, naturally weathered surface. Sorption of a constituent on the fracture surfaces of granitic or basaltic rock often is "predicted" through the use of  $K_d$ s determined from experiments performed on the crushed rock.  $K_d$  determinations rarely consider the mineralogy or physical properties of the sorbing materials, and the experiments themselves often are not described in sufficient detail.

The  $K_d$  approach inherently assumes that the sorbing mass contains an infinite number of potential sorption sites. The approach assumes that if the aqueous concentration of a constituent is increased by a given factor, the amount of sorbed constituent also will increase by the same factor, that is, the ratio of the sorbed-to-aqueous concentration will remain constant. Actual observations generally show instead that as aqueous concentrations increase, the ratio of sorbed-to-aqueous concentration tends to decrease rather than remain constant. In other words, the effective  $K_d$  tends to decrease with increasing aqueous concentrations of the constituent of interest. Following this common observation, many transport simulation computer codes now offer the possibility of simulating sorption processes using a Langmuir isotherm or Freundlich isotherm approach, instead of the linear isotherm or  $K_d$  approach. Both the Langmuir and Freundlich isotherms can simulate a decreasing ratio of sorbed-to-aqueous concentration with increasing aqueous concentration. The Langmuir isotherm also exhibits the realistic property of simulating a maximum number of sorption sites. The Freundlich isotherm does not have this capability but, in contrast to the Langmuir isotherm, the Freundlich isotherm has the capability of simulating an increasing ratio of sorbed-to-aqueous concentration with an increase in aqueous concentration. Although relatively uncommon, this behavior is sometimes exhibited by constituents undergoing ion exchange until all exchange sites are filled by the constituent. This situation occurs in the presence of another constituent that shows preferential exchange (given equal aqueous concentrations of both constituents).

These sorption models (the linear isotherm or  $K_d$  approach, the Freundlich isotherm, and the Langmuir isotherm) apply only to single components. The models do

not account for the competitive sorption by other components of the aqueous solution. The models also do not account for the aqueous speciation of the component of interest. Even though some specific aqueous species of a given component may be much more strongly sorbed than are other species of that same component, the  $K_d$ , Langmuir and Freundlich models consider only the total aqueous concentrations of the component and, therefore, ignore the thermodynamic properties of its constituent aqueous species. This major limitation is even more problematic for chemical elements with multiple oxidation states (such as U, Np, and Pu), given that different oxidation states commonly have extremely different aqueous stabilities.

The  $K_d$ , Langmuir, and Freundlich models also ignore the speciation of the sorbing surface. Although certain minerals have a relatively fixed number of sorption sites, regardless of the composition and pH of the contacting solution (notably minerals for which an ion-exchange model may be appropriate, such as certain clays and zeolites), other minerals have surface properties (such as the number of surface sites of a particular charge) that vary greatly as a function of the pH and aqueous composition of the contacting solution.

#### 5.5.1.3 Applicability of the $K_d$ approach to ground-water systems in chemical steady state

The  $K_d$  approach may adequately describe contaminant migration and reversible sorption in ground-water systems in which the aquifer regions occupied by the contaminant plume and by the background water each have uniform mineralogical and chemical compositions that remain uniform through the timescale of interest. In general, the reactive sorption of the contaminant of interest also must be adequately described by the local equilibrium assumption (LEA). That is, the reaction rate of the contaminant in a representative unit volume of the aquifer must be fast relative to its transport through that volume. If this is not the case, the system will not be described by two chemically and mineralogically uniform regions.

In a seminal paper, Reardon (1981) demonstrated that the  $K_d$  approach could not properly describe contaminant migration in ground-water systems undergoing dynamic chemical evolution and could not even properly describe contaminant migration in systems that were at chemical steady state. In systems at chemical steady state,  $K_d$ s may vary spatially but must be constant through time at any given point in the system. Most contaminated ground-water systems are not at chemical steady state and, instead, can be best described as dynamically evolving

systems in which effective  $K_d$ s will vary, not only spatially, but also during the time-scale of interest.

Reardon (1981) described a one-dimensional system in which  $^{90}\text{Sr}$ , the contaminant of interest, underwent ion exchange reactions with Ca, Na, K, and Mg, which were themselves affected by the dissolution of calcite. The dissolution of calcite was described by a kinetic model, rather than by the LEA. The LEA was used, however, to describe the ion exchange reactions. Figure 5-13 shows how the effective  $K_d$ s for  $^{90}\text{Sr}$  varied throughout the one-dimensional system, under conditions of chemical steady state, by a factor of approximately 2, as a function of the saturation index of calcite. Because the dissolution of calcite was kinetically limited (the LEA did not apply), calcite saturation was only reached approximately midway through the column. Had the calcite reacted sufficiently fast for the LEA to apply, and had initial calcite concentrations been sufficiently large so as not to be depleted anywhere in the system during the timescale of interest,  $K_d$ s would have been uniform throughout the column.

Figure 5-14 shows how the  $K_d$ s varied under conditions of dynamic chemical evolution, prior to attainment of chemical steady state. Under these conditions,  $K_d$ s varied spatially and temporally by nearly an order of magnitude.

#### 5.5.2 Advantages and limitations of speciation-based approaches in modeling sorption reactions

In contrast to computer codes that use the  $K_d$  concept and simulate the transport of only a single component, several multispecies reactive-transport codes currently exist that offer the possibility of accounting for the wide variety of chemical reactions that can affect the transport of contaminants. These codes commonly are associated with a thermodynamic data base that is used to calculate the equilibrium state of the water and contacting surfaces, minerals, and gases in the ground-water system as a function of both time and space. The codes can simulate the mass transfers of constituents between the various phases in the system that may be needed to reach a state of equilibrium at any given point and time. Some of the codes also have the additional capability of simulating the kinetic restrictions that may prevent these equilibrium states from being reached instantaneously.

The advantage of these multispecies reactive-transport codes is that in addition to the possibility of simulating more realistically the numerous complex chemical processes that may affect the behavior and fate of contaminants, the codes are based on a set of thermodynamic

constants that, in theory at least, are relatively independent of actual field conditions.

Typically, the thermodynamic constants are determined in well-controlled laboratory experiments. Although thermodynamic data describing the reaction of major cations and anions commonly present in natural water are relatively well known, at least for reactions that are sufficiently fast to have been successfully simulated under laboratory timescales, significant knowledge gaps and uncertainties exist concerning the thermodynamic properties and behavior of the elements that are of concern in contaminant transport studies. In particular, the thermodynamic properties and behavior of radionuclides (such as Am, Np, Pu and even U) are not particularly well known because of the difficulties associated with conducting accurate experiments with them.

Additionally, the thermodynamic properties of mineral surfaces are difficult to characterize in the field and even in the lab. Many uncertainties exist regarding the thermodynamic behavior of "mixtures" of surfaces and the effects caused by aging, poisoning, and recrystallization of mineral surfaces. It is also not always easy to discriminate between different processes that may be occurring, such as sorption, solid-solution formation, or recrystallization.

Finally, the simulation of chemical reactions under conditions of chemical equilibrium is often not relevant to field conditions because of kinetic limitations in the reactions of interest. Knowledge of reaction kinetics is significantly more limited and more dependent on actual field conditions than is knowledge of thermodynamic properties. Any attempt to determine reaction kinetics from field observations also is constrained by the difficulties in gaining sufficiently detailed knowledge of the physical properties of a ground-water system.

Simulations conducted with multispecies reactive-transport codes can be computationally intensive, particularly if two-dimensional or three-dimensional simulations are conducted. Unfortunately, sensitivity analyses, for which simulations must be run numerous times while only a few parameters are changed at a time, are one of the primary uses of these full-featured computer codes. Any increase in simulation complexity generally requires a significant increase in the number of simulation runs for a true understanding of the results of the simulations. Although computer time restrictions are easing, the desire to increase the complexity of contaminant transport simulations to the maximum limit of computer capabilities is always present, often to the detriment of gaining a better understanding of contaminant transport in the ground-water system being investigated.

Given these uncertainties and limitations, simple models that successfully simulate the essential properties of contaminant transport and reaction have an undeniable appeal. However, because of its many limitations, the  $K_d$  approach may be too restrictive in simulating reactive transport, and use of  $K_d$ s should be carefully examined to confirm or deny their suitability for any given field situation.

### 5.5.3 Uncertainties at the Idaho National Engineering and Environmental Laboratory site and their potential effects on simulation of radionuclide sorption and retardation

In addition to the uncertainties related to the conceptual models previously discussed, application of any of these conceptual models in simulating radionuclide transport at the INEEL site is limited by a lack of sufficiently detailed knowledge of the geology, hydrology, chemistry, and mineralogy of the site.

The chemistry of the water in the areas of radioactive waste disposal can be expected to differ significantly, particularly in terms of redox conditions, from the chemistry of the background water that remains unaffected by waste-disposal activities. The redox conditions in the areas of radioactive waste disposal can be expected to be more reducing and, therefore, generally less conducive to radionuclide transport (particularly for U, Np and Pu), than the oxygenated water which is predominant in the uncontaminated areas. The presence of steel and iron barrels and of detrital organic matter, such as cardboard and paper products, should generate reducing conditions. The distribution of redox conditions also is likely to be heterogeneous. Finally, large organic carbon concentrations in the waste disposal areas may lead to significantly enriched  $P_{CO_2}$  values for the water recharging through these areas. pH values also may differ significantly from background values. Large dissolved  $CO_3$  concentrations in the recharging water could significantly increase the aqueous stability of radionuclides such as Am, U, Np, and Pu. Unfortunately, field data allowing closer examination of these hypotheses were not available for this report.

Redox conditions in the sediment interbeds also are not well documented and probably are heterogeneously distributed. It is possible that relatively impermeable, fully saturated zones of the interbeds could contain reducing water that could impede the movement of radionuclides such as U, Np, and Pu. Rightmire and Lewis (1987a) mentioned some occasional organic-rich layers in their examination of cores from the INEEL site. Relatively impermeable zones also could contain Fe(II) miner-



als, which potentially could act as reductants for U, Np, and Pu.

In addition to the uncertainties relating to the distribution of redox conditions at the INEEL site, the distribution of reactive minerals, of sorbing surfaces, of effective porosities, and of mineral-surface-to-water ratios also is likely to be heterogeneous and to differ significantly, not just between the sedimentary interbed and basalt units, but also within the units themselves.

#### 5.5.4 One-dimensional transport simulations for U and Np

This section examines the results of some one-dimensional, multispecies reactive-transport simulations that were conducted using site and ground-water properties considered representative of the INEEL site and extends the Np and U aqueous and surface speciation results previously discussed in section 4.3.2.

##### 5.5.4.1 U(VI) transport calculations

Multispecies reactive-solute-transport simulations were conducted to examine the variability in sorption properties that might be expected at the SDA. The approach was to use the RATEQ model (Curtis, 1999) to fit one of the breakthrough curves for U(VI) transport in laboratory columns containing sedimentary interbed material (reported by Newman and others, 1995). The adsorption of U(VI) in the columns was simulated using the SCM approach. The fitted model then was used to illustrate the range in breakthrough behavior (or retardation factors) for the different INEEL ground-water samples listed in table 4-4.

##### 5.5.4.1.1 Calibration of the reactive-transport model

One of the challenges in applying SCMs to describe transport of adsorbing ions in aquifers is that it is difficult to characterize the adsorbing phase. One approach used to address this difficulty was to identify all the mineral surfaces present in the aquifer material and then sum the sorption onto all these sites. Davis and others (1998) referred to this approach as the component additivity approach. This approach requires detailed knowledge of the amount and adsorption properties of each adsorbing surface. This requirement is further complicated by the fact that most bulk phases are covered with surface coatings that have a different composition from that of the bulk phase. An alternative approach suggested by Davis and others (1998) is to use the same adsorption reactions and equilibrium equations as used in an SCM for a pure

solid but to estimate the required parameters from observed adsorption data on the more complex natural solid. These parameters include the adsorption equilibrium constants and the number of reactive surface sites. This second approach, termed the generalized composite approach (Davis and others, 1998), was used for the simulations discussed below.

For U(VI) transport, formulating the generalized composite approach was difficult because many SCMs have been proposed to describe U(VI) adsorption (table 4-1). These SCMs differ in the stoichiometry of  $H^+$ ,  $UO_2^{+2}$ , and  $CO_3^{-2}$  in the adsorption reactions and in the number and types of surface sites and competing adsorbates. To adequately calibrate the SCMs, it is preferable to consider variations in all these parameters (Kohler and others, 1996). The breakthrough curves reported by Newman and others (1995), however, were conducted only for one set of chemical conditions. Therefore, it was not possible to fully calibrate the SCM used in the reactive-transport model. For the simulations reported in this section, the SCM for U(VI) adsorption onto ferrihydrite was used and only the total number of reactive sites was varied to obtain a match to the data; all the reactions, equilibrium constants, and ratio of strong to weak sites were the same as for pure ferrihydrite (Waite and others, 1994). A more complete calibration could involve modifying the equilibrium constants. Although the ferrihydrite SCM is the most complex model listed in table 4-1, it was selected because ferrihydrite can be expected to be an important sorbing surface at the SDA (section 5.2.2).

The reactive-transport model with the ferrihydrite SCM was fitted to the U(VI) breakthrough curve observed in the laboratory and originally shown as figure 13 in the report by Newman and others (1995), and reproduced in this report as figure 5-8. This fitted model then was used to illustrate the sensitivity of retardation to variations in pH and alkalinity measured in ground water at the INEEL. Columns packed with sedimentary interbed material were used in the experiments to simulate U(VI) transport in the fitted model. There were two significant problems with this data set. First, the initial U(VI) concentrations were not reported; therefore, for the sake of illustration, a value of  $10^{-7}$  M was assumed. Second, the pH in the feed solution, which was undersaturated with respect to calcite, was 8.0, but the pH of the effluent was 8.48 and the specific conductivity also increased in the column. Speciation calculations showed that this rise in pH was consistent with equilibrating the feed solution with calcite. Because there is no way of knowing how the pH varied spatially and temporally in the column, transport simulations were conducted at a fixed pH. Simulations were con-

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ducted at pH 8.0 without calcite present and at pH 8.48 with calcite present. The two fitted breakthrough curves are shown in figure 5-15. The total site densities required to match the breakthrough curve for pH 8 and 8.48 were 1 and 2.8 mM, respectively. These values are slightly less than the value of 4.7 mM used for sand in the Cape Cod aquifer (Davis and others, 1998). Neither of the model fits reproduced the long tail illustrated by the data. One possible explanation for this long tail is that there was a small fraction of strongly sorbing sites not accounted for in the model (Kohler and others, 1996). This long tail also could be the result of other factors, including the variation in pH, slow adsorption kinetics, or adsorption from zones of immobile water.

### 5.5.4.1.2 Application of the surface complexation model to ground water at the Idaho National Engineering and Environmental Laboratory

RATEQ simulations using the SCM results fitted at both pH 8.0 and 8.48 were conducted for the 12 INEEL water samples summarized in table 4-4. These simulations neglected hydrodynamic dispersion but included approximately 80 to 120 solution and surface species, depending on whether  $\text{PO}_4$  and F were included in the simulation. In performing these simulations, it was implicitly assumed that the adsorption properties in the columns packed with the interbed materials applied to each of the 12 water samples considered. This assumption is similar to that used by Magnuson and Sondrup (1998), although it has not been tested. Figure 5-16a illustrates the range in breakthrough behavior calculated from the SCM results fitted at pH 8 for all 12 water samples. In this figure, the retardation factors are equal to the pore volumes required to elute the center of mass of the U(VI) pulse. For example, U(VI) in water from well USGS 92, is slightly retarded; the retardation factor is approximately 2 to 3. In contrast, in water from the BLR, U(VI) is moderately retarded; the retardation factor is approximately 100. The retardation factors for U(VI) in the remaining water samples range from approximately 6 to 30. Even if the water from the BLR is ignored because it is a surface water and has a low pH and large  $P_{\text{CO}_2}$ , the retardation factors for U(VI) vary by a factor of more than 10. The trend of SCM results fitted at pH 8.48 is similar to that fitted at pH 8, but the retardation factors are larger. This shift results because, at the assumed pH of 8.48, more reactive sites were required to match the breakthrough curve observed in the column experiments. Again, the retardation factors vary by a factor of 10 for the INEEL ground water. For any given water composition, the two models yield retardation factors that vary by a factor of 2 to 3.

### 5.5.4.1.3 Comparison of one-dimensional transport simulations and calculated $K_d$ s

Coincidentally, the site density of 1 mM required to match the U(VI) breakthrough in the column experiments at the assumed pH of 8 is the same as the site density used for the  $K_d$ s calculated for batch conditions listed in table 4-3. A comparison of the  $K_d$ s for the batch calculations for ferrihydrite in table 4-3 and the  $K_d$  values from the column simulations (calculated as  $K_d = R-1$ ) shows a close correspondence between the batch and column approaches. This correspondence occurs because geochemical conditions for the reactive-transport simulations were nearly constant. Specifically, initial chemical conditions in the column and boundary conditions in the feed solution were the same with the exception of  $10^{-7}$  M U(VI). The pH, therefore, remained approximately constant because calcite was ignored in the simulations for the INEEL water. Thus, the transport simulations and the batch  $K_d$  calculations were performed for the same chemical conditions. The differences in the elution order among the different water samples resulted from the variability of the chemical conditions, primarily pH and alkalinity. Overall, the retardation factors calculated from the  $K_d$ s for 1 mM ferrihydrite in table 4-3 agree well with the transport simulations. This agreement suggests that the variability in the retardation factors at the INEEL can be illustrated by considering the  $K_d$ s obtained from batch experiments.

The  $K_d$  calculated for a specific ground-water sample from a speciation model depends on the SCM used to fit the data. To examine the effect of using different SCM formulations, the SCMs for quartz, montmorillonite, goethite, and ferrihydrite were considered in greater detail. The total site density for each SCM model was varied so that the  $K_d$  equaled 20, which is approximately equal to the value observed in the Neuman column experiment (fig. 13 in the report by Newman and others, 1995). The solution composition had a pH of 8.48 and was equilibrated with calcite. Thus, the four different SCMs were forced to give the same  $K_d$ s at one solution composition that was selected to be the experimental column effluent condition. Using the site density fit just described,  $K_d$ s were calculated for the 12 INEEL water samples listed in table 4-4 and for the four different SCMs. These calculations were similar to those in table 4-3 except that the site densities for the calculations in table 5-7 were adjusted to match the column results. The results of these calculations are shown in table 5-7.

The site densities required to match the selected  $K_d$  of 20 ranged from 12 mM for quartz to 1.1 mM for goethite, reflecting the higher affinity of U(VI) for goethite. Each row in table 5-7 illustrates the range in  $K_d$ s calculated for

the different SCMs at a constant water composition. The calculated K<sub>r</sub>s for the four SCMs typically vary by a factor of 2 to 4 in most of the water samples. Larger ranges are observed for samples from the BLR and USGS 19. These larger ranges result because of the different stoichiometries in the various SCMs coupled with the larger difference in pH and alkalinity values for these water samples relative to those for the column effluent solution or for the remaining ground-water samples.

Each column in table 5-7 illustrates the range in calculated K<sub>r</sub>s for SCMs for different INEEL water samples. The results for quartz and montmorillonite SCMs are similar. For each sample, the difference in K<sub>r</sub> tends to be less than 25 percent, and the minimum, median, average, and maximum values all agree closely. For the 12 INEEL water samples, the K<sub>r</sub>s vary by a factor of 20 for these quartz and montmorillonite SCMs. Results for the two Fe phases are also similar, although for a given sample, the difference in K<sub>r</sub> for the two SCMs varies by as much as a factor of 1.8, as in the case of USGS 19. The average K<sub>r</sub> for the Fe phases is roughly twice that of quartz and montmorillonite. These differences result because of the differences in the stoichiometry of the adsorption reactions. In particular, the quartz and montmorillonite SCMs do not include the CO<sub>3</sub><sup>-2</sup> in the formation of the surface complex, whereas the goethite and ferrihydrite do include the CO<sub>3</sub><sup>-2</sup> in the surface complex (table 4-1). For the range of ground-water samples considered, the K<sub>r</sub>s vary by a factor of 24 to 31 for ferrihydrite and goethite, respectively. Given that the column experiments by Newman and others (1995) considered only one solution composition, it is impossible to evaluate whether CO<sub>3</sub><sup>-2</sup> may be a part of the adsorbed complex for the INEEL sediments. Finally, the ranges in K<sub>r</sub>s in table 5-7 were obtained by matching a site density that gave a K<sub>r</sub> of 20 for a pH 8.48 water in equilibrium with calcite. Similar ranges in K<sub>r</sub>s would have been obtained if the pH had been 8, but the absolute K<sub>r</sub>s would have been smaller.

The calculated range in K<sub>r</sub>s of 20 to 30 for U is considerably larger than the range calculated for Np (factor of 1.3) and Pu (factor of 2.0) (table 4-1). This small factor difference for Np can be explained by comparing the solution chemistry. The aqueous speciation chemistry for U(VI) is significantly more complex than for Np(V). Figure 4-2 shows that at atmospheric  $P_{CO_2}$ , and in the pH range of 7.5 to 8.4, the species UO<sub>2</sub>(OH)<sub>2</sub>, UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>-2</sup>, (UO<sub>2</sub>)<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>3</sub><sup>-</sup>, and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>-4</sup> are present at greater than 10 percent of the total concentration at certain pH values. A similar plot of Np(V) aqueous speciation in a report by Turner and others (1998) shows that the NpO<sub>2</sub><sup>+</sup> ion is the single dominant species up to pH 8.5,

where the NpO<sub>2</sub>CO<sub>3</sub><sup>-</sup> species then becomes important. The adsorption behaviors of U(VI) and Np(V) are also different. At pH values above 7, U(VI) log K<sub>r</sub>s decrease nearly linearly with pH (fig. 4-7) because of the formation of soluble U(VI) CO<sub>3</sub> complexes. Adsorption of Np(V) also decreases because of the formation of soluble CO<sub>3</sub> complexes, but the trend of decreased adsorption starts at pH values of approximately pH 8 in the case of montmorillonite (Turner and others, 1998). Finally, the SCM for Np(V) does not include ternary surface complexes involving CO<sub>3</sub>, although their existence has been postulated (Turner and others, 1998).

In summary, the reactive-transport calculations for U(VI) presented in this section illustrate that *if the geochemical conditions are constant*, reactive-transport simulation results can be approximated by a single K<sub>r</sub>. Over the INEEL site, *geochemical conditions are not constant*; therefore, K<sub>r</sub>s vary for the different water compositions. There is no clear explanation for the variations in the aqueous geochemistry; therefore, without additional detailed geochemical data, fully coupled reactive-transport simulations are not warranted. On the other hand, both the transport calculations and the batch calculations illustrate that, given the current state of our understanding of the SDA and models of adsorption properties, the calculated K<sub>r</sub>s for U(VI) vary by a factor of 20 or more for each selected SCM just because of the variation in water composition. Adsorption properties at the SDA also may vary because of the variation in surface properties, including both the affinity for the actinide and the concentration of adsorbing sites. These variations have not been quantified and represent a gap in the data. A comparison of four different SCM results show that K<sub>r</sub>s vary by a factor of as much as 70.

#### 5.5.4.2 Np transport calculations

Np and Pu one-dimensional transport simulations were conducted with version 2.038 of the USGS computer code PHREEQC (Parkhurst and Appelo, 1999). Confirming results previously discussed in sections 4.3.2, Np sorbs much more strongly than Pu; and under the specific conditions of those transport simulations, Pu was not retarded significantly and, therefore, will not be discussed further. This result does not imply that Pu transport will not be retarded at the INEEL site. A greater concentration of sorbing sites (an increase by a factor of 2,000 was suggested reasonable in section 4.3.2), and the presence of possible reducing environments could cause significant retardation of Pu transport at the site. Nevertheless, many of the conclusions derived from the Np transport results presented in this section can be expected to apply to potential Pu transport.